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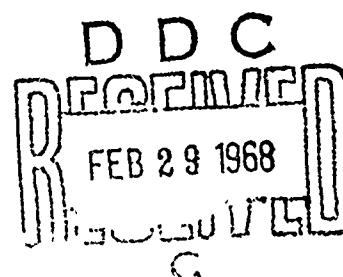
SEPARATORS FOR HIGH-RATE, NON-RESERVE ZINC-SILVER OXIDE BATTERIES

FINAL REPORT

BY

A. HIMY

JANUARY 1968



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ASTROPOWER LABORATORY, DOUGLAS AIRCRAFT COMPANY

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SEPARATORS FOR HIGH-RATE, NON-RESERVE
ZINC-SILVER OXIDE BATTERIES

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PREPARED BY

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ABSTRACT

This report covers a program on the investigation of separator materials for high rate, nonreserve zinc-silver oxide batteries capable of operating at temperatures as high as 165°F.

The films were obtained by blending an inorganic material (previously used to make separators for secondary silver-zinc cells) with an organic binder.

The program consisted of four tasks:

1. Characterization of Inorganic Materials

Two basic materials, designated 3355-25 and 3420-09, were selected to make separators which were used as controls and were evaluated for resistivity, inertness in KOH at 77°F and at 165°F, silver and zinc diffusion rates and resistance to oxidation by silver saturated KOH solution. Although both materials showed close characteristics, the material 3420-09 was selected for its greater stability in KOH at 165°F.

2. Initial Composite Film Preparation and Characterization

For blending, two types of organic binders, K and P, and three procedures were used:

Procedure A: The film was cast on glass or Teflon.

Procedure B: A slurry was introduced in a porous thin matrix.

Procedure D: The silver electrode was dipped in the liquid formulation, resulting in a dip-coated electrode.

The results favored the binder P as more stable. The resistivities of the most promising films were in the range of 7 to 15 ohm-cm and the silver ion diffusion rates were lower than those obtained with the inorganic separators on the previous task.

3. Final Composite Film

This task was aimed at continued improvement and evaluation of certain films selected from the previous task. One formulation was found worth using by two procedures, A and B, and the membranes prepared by these two procedures were extensively evaluated for uniformity and fabrication reproducibility.

4. Cell Testing and Evaluation

Several wet stand tests were run on cells of various separator designs and combinations. All cells were identical in electrode design and had

1-Ah nominal capacity. The separator system used involved exclusively silver electrode dip-coating, zinc-bagging, or both. All systems were potentially good over a period of 3 months at room temperature. At 165°F, the maximum reliability was attained by combining Ag dip-coating and Zn bagging. Loss of capacity at 165°F was traced to zinc capacity loss rather than separator deficiency and shorting.

FOREWORD

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Section 1

SUMMARY AND CONCLUSIONS

This report covers an investigation of separator materials for high rate, nonreserve zinc-silver oxide batteries capable of operation at temperatures as high as 165°F.

The program involves the use of inorganic separator materials developed at this laboratory over the past five years. Inorganic materials are blended with stable organic polymeric binders to form composite films. It is thereby possible to obtain thin films possessing the high ionic conductance of the inorganic granules and their high stability with the film-forming characteristics and stability of the organic binder.

The program plan consisted of four distinct tasks. The following is a detailed outline of significant results obtained:

Task I: Characterization of Inorganic Materials

Two of the most promising inorganic materials, 3355-25 and 3420-09, were selected for this study and separators about 25 mils thick were made at different porosity levels.

- (a) Both types manifested comparable resistivities in 31% KOH at 77°F in the range of 10 to 15 ohm-cm.
- (b) The 3420-09 type separators were particularly stable at 77°F and at 165°F over the one-month test period.
- (c) Silver diffusion rates appear to be unaffected by separator porosity at the low levels selected. On the other hand, zinc ion diffusion rates increased slightly with increased porosity.
- (d) Resistance to oxidation by soluble silver species in KOH was good over the one-month test period. At 77°F, the amount of silver picked-up was negligible, whereas at 165°F it was in the range of 1 mg/in².

It was decided to employ the granulated 3420-09 inorganic material exclusively in the development of composite inorganic-organic films because of its more uniform behavior in the stability tests.

Task II: Initial Composite Film Preparation and Characterization

Different film compositions comprised of 3420-09 inorganic materials and one of two kinds of organic polymer binders K and P were prepared by the following three basic procedures:

Procedure A: The film is cast on glass or Teflon.

Procedure B: A slurry is introduced in a porous thin matrix.

Procedure D: The silver electrode is dipped in the liquid formulation, resulting in a dip-coated electrode.

The concentration of the inorganic component ranged from 75% to 95%. The films obtained were generally in the range of 5 to 10 mils.

- (a) The resistivities of the most promising composite films in 31% KOH at 77°F were in the range of 7 to 15 ohm-cm.
- (b) Dimensional stability tests indicated that films using binder P were particularly inert in KOH over the one-month test period, even at 165°F.
- (c) Silver ion diffusion rates for the best composite films were generally lower than those obtained for the inorganic separators. Zinc ion diffusion rates were comparable.
- (d) Resistance to oxidation by soluble silver species in KOH at 77°F and 165°F, determined by the amount of silver pick-up, was higher for the composite films than for the inorganic separators. However, the P binder composite films picked up less silver than K binder types.

At the end of this task, it was decided to further the development of composite films using exclusively type P binder, as prepared by procedures A, B and D.

Task III: Final Film Fabrication and Evaluation

This task was aimed at continued improvement and evaluation of a formulation selected from the previous task and used to make films by procedures A and B with particular emphasis on using a small amount of plasticizer sufficiently inert under the test conditions. These films were constantly evaluated for resistivity, silver and zinc ion diffusion at 77°F and 165°F, and resistance to oxidation. Silver ion diffusion rates were measured by three different methods.

Task IV: One Ampere-Hour Zinc-Silver Oxide Cell Tests and Evaluation

Several wet stand tests were run on cells of various separator designs and configurations. All cells were identical in electrode design and had 1-Ah nominal capacity. The separator system used involved exclusively silver electrode dip-coating, zinc bagging, or both. All systems were potentially good over a period of 3 months at 77°F. At 165°F, the maximum reliability was attained by combining Ag dip-coating and Zn bagging. Loss of capacity at 165°F was traced to zinc capacity loss rather than separator deficiency and shorting.

In summary, the feasibility of the approach has been demonstrated in the following manner:

- (a) Three-mil composite films are easily made.
- (b) Their resistivity ranges from 10 to 15 ohm-cm.
- (c) They have good dimensional stability up to 165°F.
- (d) Compared with the inorganic separators that have been used in secondary cells and have shown long cycling capability,* the silver ion diffusion rate is lower, the zinc ion diffusion rate is equivalent, and the silver pick-up is slightly higher.

*Arrance, F. C., Program to Develop an Inorganic Separator for a High Temperature Silver-Zinc Battery, Douglas Report SM-48461-F, Astropower Laboratory, Douglas Aircraft Company, Newport Beach, California, June 1967.

Section 2

INTRODUCTION

The principal problem with separators for high rate, nonreserve, zinc-silver oxide batteries capable of operating at temperatures as high as 165°F is chemical instability. The reactive nature of the electrodic components, as well as the required use of caustic electrolyte, are the causes. Since 1962, this laboratory has been developing ceramic inorganic separators that are inert in severe environments while possessing low resistances.* These separators are prepared from synthetic as well as naturally occurring alkali-alkaline earth alumino silicates. The final product has a specific porous microstructure designed to permit the passage of hydroxyl ions while inhibiting the transfer of silver and zincate ions. Simultaneously, the ceramic bonds of the separator structure make it inert to attack by silver oxide.

To achieve some degree of flexibility and reduce the separator thickness to 5 mils, this laboratory has developed composite inorganic-organic separator systems as well. These systems are prepared as composites of inorganic components with inert organic polymeric binder. Since the inorganic component is present in at least 75% by weight, the essential beneficial aspects of this material are retained. The sole function of the organic component is to bond the inorganic material together.

The purpose of this program is to investigate separator materials for high rate, nonreserve, zinc-silver oxide batteries for obtaining a readily producible film, having the following properties:

1. Electrical Resistance — this is not to be above that of untreated PUDO-300 Cellophane (about 7-9 ohm-cm).
2. Inertness to Electrolyte — the separator should be unaltered by 31% aqueous KOH solution over long periods of time (three to five years) from -40°F to +165°F.
3. Impermeability to Ions — the separator should be impermeable to silver and zincate ions over the temperature range -40°F to +165°F. This property is considered to be not only a function of pore size but also polar and steric factors.

* ibid.

also: Berger, C., Arrance, F. C., and Taylor, A. D., Inorganic Separator for High Temperature Silver-Zinc Battery, NASA CR-54749, Douglas Report SM-46220-F, Astropower Laboratory, Douglas Aircraft Company, Newport Beach, California, September 1965.

4. Thickness — it is preferred that the thickness should not exceed 5 mils.
5. Resistance to Oxidation — the separator material should be resistant to oxidation in the presence of silver oxides.

In order to derive the separator material best capable of meeting the above requirements, a program based on the following four tasks was initiated.

TASK I — Preparation and Characterization of Inorganic Materials

TASK II — Initial Film Preparation and Characterization

TASK III — Final Film Fabrication and Evaluation

TASK IV — One-Ampere Hour Zinc-Silver Oxide Cell Tests and Evaluation

The program was concerned with selecting an optimum inorganic material and formulating several inorganic-organic composites, accompanied by a series of evaluations designed to satisfy the requirements outlined above. Finally, the most favorable systems were subjected to actual cell tests to complete the evaluation.

This report provides a description of the results obtained during the course of the program. Separator mechanistic interpretations are also presented and experimental procedures are described.

Section 3

THE MECHANISM OF SEPARATOR BEHAVIOR

These discussions apply to inorganic materials. To date, our understanding of separator behavior has been based on physical tests which have included microscopic observations. Optimum separator behavior in a nonreserve primary zinc-silver oxide cell exists when there is maximum resistance to the migration of silver and zincate ions on stand while, simultaneously during discharge, there is minimum resistance to the migration of hydroxyl ions from cathode to anode.

It was recognized early in the development of ceramic separators that lower resistivities of the order of 10 ohm-cm in 31% KOH at 77°F could be achieved. Microscopic analysis extending down to the ultra-fine structure indicates that total separator porosity was due to the following types of pores, listed in descending relative order of pore size.

1. crystallographic defects
2. intergrannular channels
3. intercrystalline channels
4. crystallographic (intracrystalline) channels.

From their more frequent, widespread occurrence, it was evident that the major portion of the contribution to the overall separator porosity was that due to the intercrystalline and crystallographic channels where pore size is at the Angstrom level.

Therefore, it was evident that composite separators comprised of inorganic material at the micron particle size level with inert organic binder, the latter at a concentration $\leq 25\%$, could result in feasible films. By the start of the current program, some films of this type had been prepared and evaluated. It was found from resistivity data that our approach was valid.

Efforts on the mechanism of separator behavior are continuing. The lowest resistivity appears to be achieved when the migration of ions occurs through a liquid phase mechanism through the pores and channels of the separator matrix. The mechanism is aided by absorption of solvent molecules on the sides of the pores. Such adsorption is governed by electrostatic as well as steric factors. Consequently, the conductance mechanism of separators is not governed by pore size alone. For example, it was demonstrated* during studies performed at this

*Strier, M. P. and Littman, F. E., Inorganic Separators for Nonaqueous Electrolyte Batteries, presented at the Spring Meeting of the Electrochemical Society, May 7-12, 1967, Dallas, Texas, Douglas Paper 4294.

laboratory in polar, nonaqueous media that an increase in separator resistivity occurred at higher temperatures. This was attributed to increasing migrating ion collisions with the walls of the channels resulting from desorption of the solvent molecules from these walls.

Ideally, the function of the separator material is to permit the passage of hydroxyl ions while preventing the passage of silver and zincate ions. The separator material possessing the proper network of channels involving pore size, tortuosity and polar forces could accomplish this goal to a high degree. The large variety of inorganic compositions available coupled with the wide versatility of mechanical structures attainable from ceramic processing techniques are conducive to producing worthwhile ceramic structures. A number of ceramic compositions have been prepared here. Two of the most favorable systems, 3355-25 and 3420-09, were selected for initial screening tests constituting Task I of this program. The results of these tests led to selecting the better system for formulation into composites with organic binder.

Section 4 WORK PERFORMED

4.1 TASK I: PREPARATION AND CHARACTERIZATION OF INORGANIC MATERIALS

The prime inorganic separators selected had the designation 3355-25 and 3420-09. They are fabricated from 100% inorganic materials (ceramic type) into square shapes of approximately 2" x 2" x 0.025". The objective was to characterize both types in terms of resistivity, inertness in KOH, impermeability to silver and zincate ions and resistance to oxidation in order to select one for incorporation in an inorganic-organic composition as called out by Task II.

Specifically, the tests applied were in order:

- (a) determination of physical characteristics (dimensions, mass, porosity, transverse strength),
- (b) electrical resistivity in 31% KOH at 77°F.,
- (c) inertness in KOH at 77°F and 165°F,
- (d) silver and zincate diffusion rates at 77°F,
- (e) silver pick-up at 77°F and 165°F, and
- (f) microstructural analysis.

Because the changes noted at 77°F are insignificant and the extent of these changes decreases with decreasing temperature, measurements at very low temperatures (-40°F) were not considered useful.

Table I gives a list of the specific magnitudes measured or calculated, with their legend and their test conditions. The symbols will be consistently used throughout this report.

4.1.1 Physical Characteristics

For each inorganic material, 3355-25 and 3420-09, three and two levels of porosity, respectively, were selected. On each one, three sample pieces (approximately 2" x 2" x 0.025") were submitted to physical measurements to determine their dimensions, weight, water pick-up or water absorption (percent of dry weight), corresponding volume porosity (void percentage of total volume), and transverse strength.

The measurements were performed with calibrated calipers and analytical balances. The water absorption is done by soaking the specimen in water under vacuum at 29 inches Hg for one-half hour, blotting the surfaces dry and weighing.

TABLE I
DETERMINATION OF SEPARATOR
CHARACTERISTICS BY MEASUREMENTS

1. Physical

Description	Unit	Symbols
Thickness	mils	t
Area	cm ²	A
Volume	cm ³	V
Mass	g	m (m' with water)
Water Absorption	%	$a_o = \frac{m' - m}{m} \times 100$
Porosity	%	$p_o = \frac{m' - m}{m} \times 100$
Modulus of Rupture	psi	M

2. Electrical:

Resistivity in 31% KOH

3. Inertness in KOH:

Measurement of dimensions and KOH wet mass after 7, 15, 30 days immersion in KOH at 77°F and 165°F.

4. Impermeability to Ions:

Silver diffusion rate: a (mg-mil/in²-hour)
Zincate diffusion rate: b. 10⁻⁵ (moles-mil/in²-minute)

5. Resistance to Oxidation

Determined by silver pick-up c in mg/in² of separator material immersed in a silver ion saturated solution of 31% KOH at 77°F and 165°F over 30 days.

The same samples are dried to constant weight then used in the KOH immersion test (Paragraph 4. 1. 3).

Transverse strength measurements were performed by the equipment and procedure given in Appendix A. 2. The measurements are performed and specimens 0.500 ± 0.001 inch wide. Samples are broken on the testing machine and the modulus of rupture is calculated as shown.

The averages and results are given in Table II.

4. 1. 2 Resistivity in KOH

The apparatus and procedure for determining resistivity under A. C. conditions is given in Appendix A1. The separator samples were vacuum impregnated with 31% KOH solution by applying a vacuum of 29 inches Hg for 30 minutes. Generally, it was found that the sample was sufficiently wetted by this treatment for the resistivity to remain nearly constant over the first 24 hours of soaking.

The results of resistivity measurements are given in Table III where the averages are representative of at least three determinations with the average deviation being within $\pm 10\%$. It had become apparent during the course of dimensional stability tests on both types of ceramics that the 3420-09 material was more stable in 31% KOH solution. The 3420-09 samples were stored in 31% KOH solution under two kinds of thermal conditions. In one, the sample was kept at 77°F for 15 weeks; in the other, the samples were kept at 165°F for one month, followed by 11 weeks at 77°F . The changes in resistivity seem negligible, whereas greater changes occur for the 3355-25 samples which had been stored for much shorter periods of time.

4. 1. 3 Inertness in KOH

The stability tests were performed in the following manner. Three two-inch square samples were kept immersed in 31% KOH solution at 77°F and 165°F . The following measurements on air-dried samples were made initially - area, thickness, weight and porosity (see Paragraph 4. 1. 1). The samples were then soaked in 31% KOH. Initial saturation with KOH was achieved by vacuum impregnation at 29 inches of Hg. After the 7, 15 and 30-day immersion periods, measurements were made on the KOH wet test specimens. The results are summarized in Table IV.

The two different 3420-09 separators appear to manifest excellent dimensional stability during the one-month stand tests at both 77°F as well as at 165°F . However, 3355-25 separators at the higher porosity ranges, I-AL-1 and I-AL-2, became too fragile before the end of the 30-day period to permit completion of their evaluation. The overall

TABLE II

TASK I
100% INORGANIC SEPARATORS
PHYSICAL CHARACTERISTICS - DRY

Material	Sample Designation	A cm ²	t mils	m (g)	a _o (%)	p _o (%)	M (psi)
3355-25	I-AL-1	28.9	21	3.12 - 3.19	20.9	42.5	7,000
	I-AL-2	24.6	26	3.73 - 3.76	15.8	36.3	8,000
	I-AL-3	23.5	25	3.65 - 3.70	11.6	28.4	12,000
3420-09	I-OL-1	24.1	26	3.98 - 4.01	7.9	19.8	10,000
	I-OL-2	28.0	26	3.79 - 4.05	15.7	33.1	7,100

TABLE III

TASK I
100% INORGANIC SEPARATORS
RESISTIVITY IN 31% KOH

Material	Sample Designation	Water Absorption	Original	After 15 Weeks at 77°F	After 4 Weeks at 165°F and 11 Weeks at 77°F
3355-25	I-AL-1	20.9%	10.0 ohm-cm	NOT TESTED*	NOT TESTED*
	I-AL-2	15.8%	13.0 ohm-cm		
	I-AL-3	11.6%	15.1 ohm-cm		
3420-09	I-OL-1	7.9%	30.9 ohm-cm	25.5 ohm-cm	24.7 ohm-cm
	I-OL-3	10.0%	21.9 ohm-cm	} NOT TESTED	} NOT TESTED
	I-OL-4	12.0%	15.9 ohm-cm		
	I-OL-2	15.7%	10.5 ohm-cm	9.8 ohm-cm	10.8 ohm-cm

* Degraded (See Table IV)

TABLE IV

TASK I
100% INORGANIC SEPARATORS
INERTNESS IN 31% KOH (MEASUREMENTS DONE WET)

Material	Sample Designation	Days on Stand	77°F				165°F			
			A cm ²	t mils	m grams	Po %	A cm ²	t mils	m grams	Po %
3355-25	I-AL-1	0	28.9	21	3.96-4.04	42.1	28.9	21	3.86-4.02	40.1
		7	28.9	21	3.96-4.05	42.2	*	*	*	*
		15	28.9	21	3.95-4.04	41.9	*	*	*	*
		30	*	*	*	*	*	*	*	*
	I-AL-2	0	24.6	26	4.44-4.47	33.2	24.6	26	4.40-4.58	34.8
		7	24.6	26	4.50-4.53	36.1	24.6	26	4.39-4.56	33.7
		15	*	*	*	*	*	*	*	*
		30	*	*	*	*	*	*	*	*
	I-AL-3	0	23.5	25	4.25-4.33	31.6	23.6	25	4.24-4.44	32.9
		7	23.5	25	4.25-4.30	30.8	23.6	25	4.23-4.40	31.9
		15	23.6	25	4.23-4.29	30.5	23.6	25	4.18-4.34	29.1
		30	23.5	25	4.25-4.30	30.9	23.6	25	4.22-4.39	31.1
3420-09	I-OL-1	0	24.1	26	4.34-4.41	18.5	23.9	26	4.27-4.39	18.8
		7	24.1	26	4.38-4.44	20.0	23.9	26	4.27-4.41	19.2
		15	24.1	26	4.38-4.44	20.3	23.9	26	4.26-4.40	18.7
		30	24.1	26	4.38-4.44	20.0	23.9	26	4.28-4.42	19.6
	I-OL-2	0	28.0	26	4.58-4.87	33.1	28.0	26	4.73-4.81	34.1
		7	28.0	26	4.57-4.87	33.2	28.0	26	4.70-4.80	33.2
		15	28.0	26	4.57-4.87	33.1	28.0	26	4.68-4.78	32.4
		30	28.0	26	4.56-4.85	32.4	28.0	26	4.69-4.79	32.8

* Test discontinued; samples not suitable for further testing.

evaluation of Table IV appears to favor the I-OL series as more stable than the I-AL series.

4. 1. 4 Impermeability to Ions

A limited number of additional tests were performed on the samples, particularly the 3420-09 material for further correlative purposes. These tests, consisting of silver diffusion and zincate diffusion, had been specified for the inorganic-organic composites and will be described in greater detail in Section 4. 2 and Appendix A. The results obtained for the inorganic materials are summarized in Table V.

1. Silver Diffusion

The apparatus, procedure and method of calculation are described in Appendix A. Measurements were performed over a six-hour period with readings of the amount of silver diffusion as ascertained by colorimetric analysis taken at two-hour intervals. There does not appear to be any correlation between silver diffusion rate and separator porosity, at the low porosity levels selected.

2. Zinc Diffusion

The apparatus, procedure and method of calculation are described in Appendix A. The higher porosity 3420-09 separators (I-OL-2) manifest higher zinc diffusion rates than the lower porosity 3420-09 separator (I-OL-1). However, the 3355-25 (I-AL-3) separator manifests a significantly higher zinc diffusion rate, while its porosity is actually lower than that of the I-OL-2 separators.

4. 1. 5 Resistance to Oxidation

The procedure for performing this at both 77°F and 165°F is given in Appendix A. Measurements were performed after 7, 15 and 30 days exposure of the sample in 31% KOH solution saturated with silver oxide. The results given in Table VI indicate no significant differences between the two 3420-09 samples.

4. 1. 6 Microstructural Analysis

Electron micrographs of polished surfaces of a 3420-09 separator (I-OL-1) and a 3355-25 separator (I-AL-3) are shown in Figures 1 and 2, respectively. The grain size of the 3420-09 separator appears to be larger than that for the 3355-25 separator. In the electron micrograph of the 3355-25 sample, macropores are depicted as large channels between the sintered particles or polycrystalline grains. Several channels are pointed out by arrows. Micropores of crystallographic dimensions are shown under the arrows in the upper field of the electron

TABLE V
TASK I
100% INORGANIC SEPARATORS
IMPERMEABILITY TO IONS AT 77°F

Material	Sample Designation	Water Absorption (%)	Silver Diffusion			Zincate Diffusion		
			Specific mg-mil/in ² -hr	Absolute mg/in ² -hr		Specific moles-mil/in ² -min	Absolute moles/in ² -min	
				Reading	Average		Reading	Average
3355-25	I-AL-3	11.6	NOT TESTED*				10.6 11.3	11.0
3420-09	I-OL-1	7.9		0.31 0.25 0.15			1.65 2.33 1.33	
	I-OL-3	10.0			0.24		1.33	1.77
	I-OL-4	12.0					2.95 2.11	2.53
	I-OL-2	15.7		0.24 0.24 0.15 0.18			5.63 3.67	4.65
					0.20		6.75 3.28	5.02
								0.19

The following test was run at 165°F

3420-09	I-OL-3	10.0	0.287 0.287	0.287	0.012
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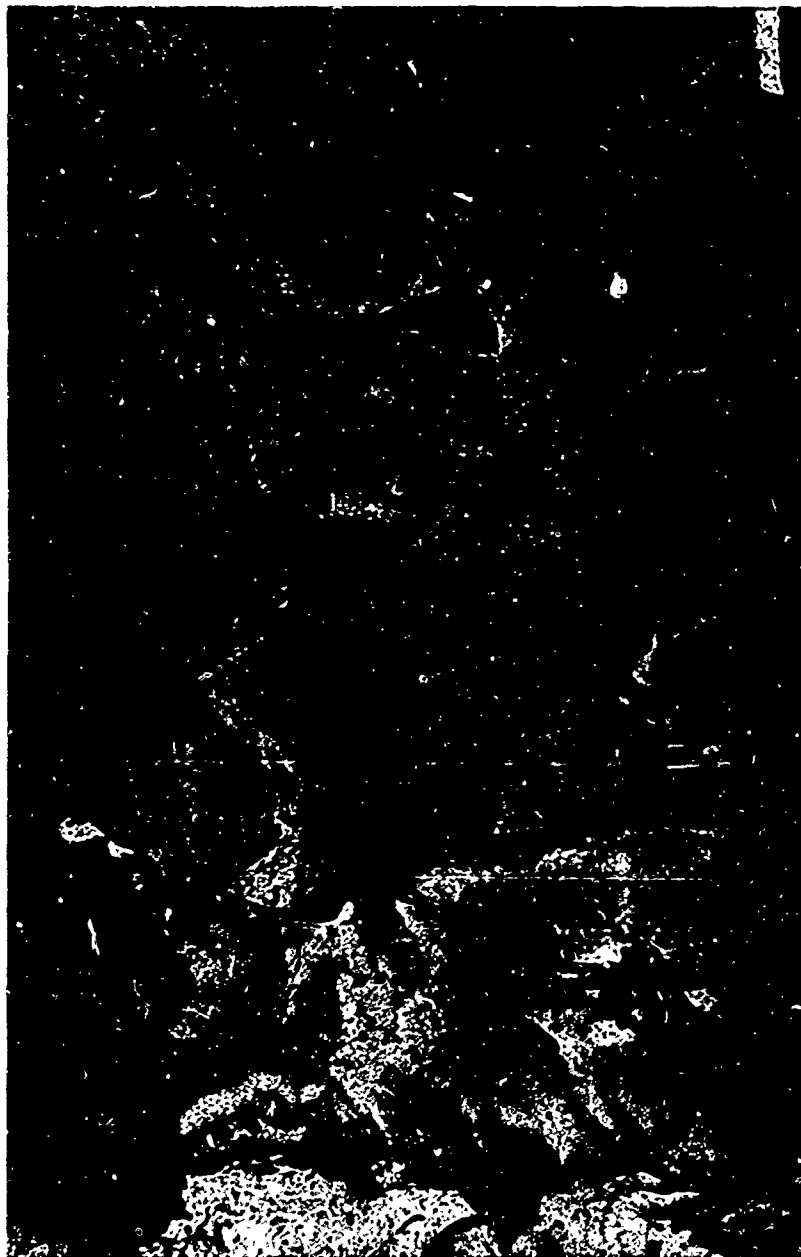
*Findings on material degradation (Table IV) made tests unnecessary.
NOTE: Zincate diffusion rate = $b \times 10^{-5}$, reported as \underline{b}

TABLE VI

TASK I

100% INORGANIC SEPARATORS
RESISTANCE TO OXIDATION (Ag PICK-UP)

Material	Sample Designation	Days on Stand	77°F			165°F		
			Absolute mg/in ²		Specific mg/in ² -mil	Absolute mg/in ²		Specific mg/in ² -mil
			Readings	Average	Average	Readings	Average	Average
3355-25	I-AL-3	7	0			0		
			0	0	0	0	0	0
		15	0			0.29		
			0	0	0	0.29	0.29	0.01
		30	0			0.87		
			0	0	0	0.86	0.86	0.04
3420-09	I-OL-1	7	0			0		
			0			0.57		
			0	0	0	0.86	0.48	0.02
		15	0			1.15		
			0	0	0	0.86	1.00	0.04
		30	0.14			1.69		
			0.14	0.14	0.01	1.71	1.70	0.07
	I-OL-2	7	0			0.72		
			0	0	0	0.72	0.72	0.03
		15	0			1.42		
			0	0	0	1.15	1.28	0.05
		30	0.12			1.71		
			0.12	0.12	0.01	1.47	1.59	0.06



CSM

Figure 1. Electron Micrograph of a Polished Surface of
the Interior in Separator 3420-09.
Magnification 11,000 X



03101

Figure 2. Electron Micrograph of a Polished Surface of
the Interior of Separator 3355-25.
Magnification 11,000X

micrograph in Figure 1. The size of the sintered grain varies between one and five microns. The channels may surround an entire grain, but show a maximum width of about one micron. They may even be larger in regions where three or four grains meet. A rich microporosity is also indicated on the channel surfaces.

In the electron micrograph of the 3420-09 separator (Figure 1), there is a more intricate, fine structure than for the 3355-25 separator. This means that the former has a higher percentage of micropores than the latter. The defect-rich structure of the 3420-09 material appears to cause a pronounced fine structure on the internal surfaces and shows a multitude of spacings above crystallographic dimensions. Overall, the 3355-25 material is characterized by larger intergranular channel spacings than those existing in the 3420-09 separator. This could account for the significantly higher zinc diffusion rates of the 3355-25 separator.

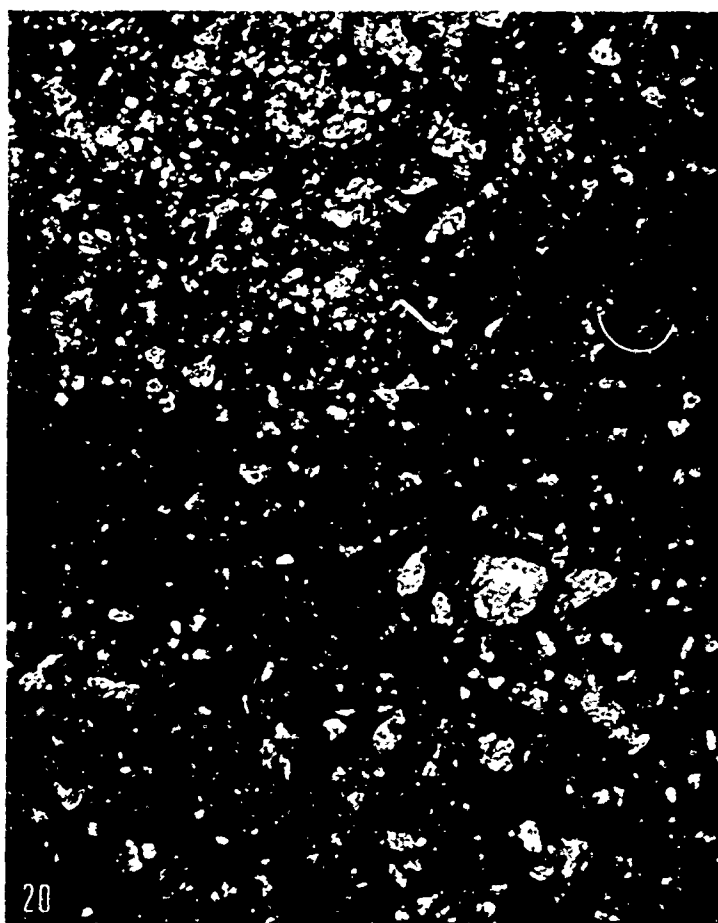
Concentrating on the 3420-09 material, photomicrographs of the surface studies of separator samples at 10% and 20% porosity, are shown in Figure 3. Note the large grain size and intermediate material of low reflectivity that is indicative of high porosity in the sample with 20% porosity. In the sample with 10%, there is significantly smaller grain size and a high light reflectivity over the entire surface. Photomicrographs of 3420-09 samples, depicting cross sections where the porosity is outlined through methylene blue staining are shown in Figures 4 and 5.

4.1.7 Inorganic Material for Film Formulation

The final selection of inorganic material for use in the composite formulation during the remainder of the program was based on overall performance of three samples of both types of materials. Because two of the three 3355-25 samples manifested some instability in 31% KOH solution during the 30-day stand period, it was decided to use the 3420-09 material. All of the 3420-09 samples showed good dimensional stability under these test conditions. One exception was noted in the silver degradation test at 165°F, i. e., the one surviving 3355-25 sample (I-AL-3) showed approximately one-half the amount of degradation manifested by the 3420-09 samples by the end of the 30-day period. However, the 3355-25 manifested significantly higher zincate diffusion rates and less favorable microstructural characteristics based on wider intergranular channels and less well-defined fine structure.

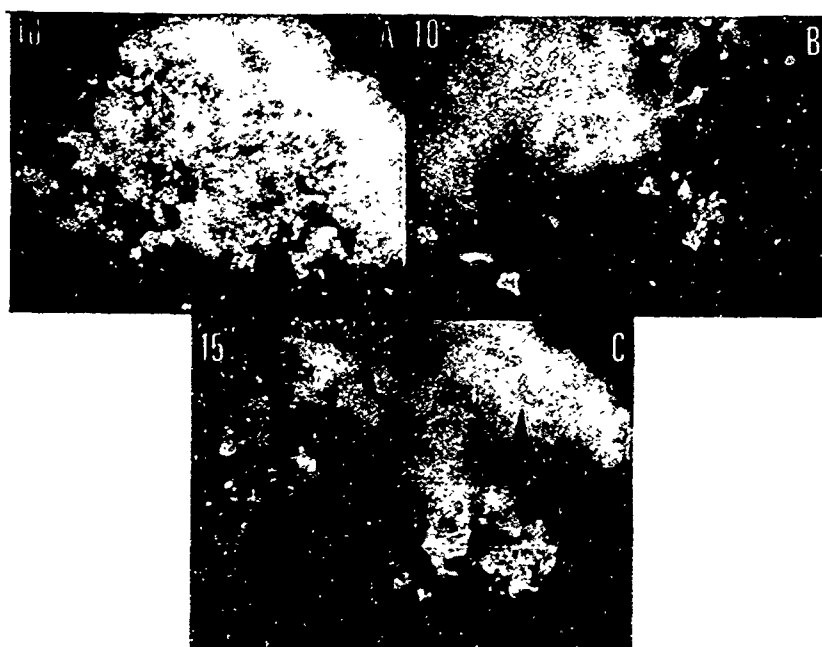
4.2 TASK II: INITIAL FILM PREPARATION AND CHARACTERIZATION

The purpose of this task was to prepare and evaluate several composite formulations in order to be able to select the most promising system for more detailed study and optimization. The inorganic material selected from the results of Task I was the material coded 3420-09. In this task,



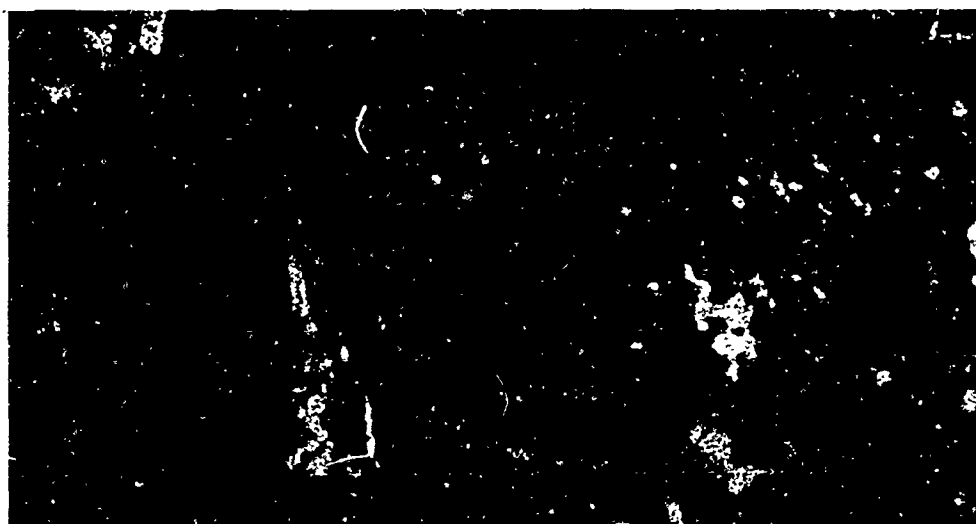
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Figure 3. Photomicrographs of Surface Structure in 3420-09 Separators With Estimated Porosity of 10 and 20% Respectively. Note large grain size and intermediate material of low reflectivity, that is indicative of high porosity in sample 20%. Note the significantly smaller grain size and a high light reflectivity over the entire surface in sample with 10% reported porosity. Magnification 450X



63563

Figure 4. Photomicrographs (Reflected Light) Depict Methylene Blue Penetration Patterns on Separator Cross Sections. Fracture surfaces were examined, therefore certain regions only are well focused. Exterior surface of separators marked ee in each micrograph, penetration direction shown by arrow. The dark color displays blue stained regions. Note the low penetration in most areas (A) of sample 10%, an occasional high porosity region as in photomicrograph B. The path in B, exceptional in sample 10%, is more characteristic of sample 15% as shown in C. Magnification 450X



63269

Figure 5. Photomicrographs of Methylene Blue Penetration in Individual Grains Showing Selected Staining. Certain crystallographic planes and defect regions are easily accessible to the stain molecules. Magnification 2,300X

two types of organic binders have been used, K and P, with minor modifications as to their grade and three different procedures have been employed in the preparation of composite film.

Procedure A: Membrane

The five essential steps involved are as follows:

- Mixing
- Casting
- Curing
- Drying
- Post-treatment

The 3420-09 material was added with stirring to a solution of organic polymer binder and plasticizer (if necessary) in polar solvent. The latter was ground down to micron particle size. Then the homogeneous mixture was cast either on a glass or Teflon-coated plate. After air drying at 77°F, the film was cured at elevated temperature (150°F to 350°F) for 15 minutes. Occasionally, it was found expedient to release the film by soaking it in water.

Procedure B: Slurry in Matrix

The porous organic matrix is suspended in a slurry of 3420-09 material in polar solvent in which the organic binder has been dissolved. Next, the coated matrix is air-cured at 250°F for 15 minutes.

Procedure D: Dip Coated Electrodes

The procedure is the same as for Procedure B, except that an uncharged silver electrode is suspended in the inorganic material-organic binder-solvent mixture.

The evaluations were performed by methods and with equipment described in Section 4. 1 and Appendix A.

The only significant screening tests possible for films prepared by Procedure D, other than actual zinc-silver oxide cell tests, would be silver diffusion cell tests, as described below in Section 4. 2. 3.

Tables VII, VIII, and IX give a list of all composite (inorganic-organic) film formulations and their physical appearance, which served as a rough screening. The resistivity test and the inertness in KOH test served also as concurrent means for further screening. These two tests narrowed down the choice of formulations worth further investigation.

TABLE VII
TASK II
LIST OF COMPOSITE FILMS
PREPARED BY PROCEDURE A

Film Designation	Inorganic Content, %	Organic Binder %, Type	Plasticizer %, Type	Physical Appearance
A-OL-1	75	25, K-B	10, D	Weak
A-OL-2	75	25, K-B		Weak
A-OL-3	75	25, K-B		Good
A-OL-4	90	10, K-A		Weak
A-OL-5	90	10, K-A		Good
A-OL-6	95	5, P		Weak
A-OL-7	90	10, K-B		Good
A-OL-8	90	10, K-A		Good
A-OL-9	80	20, P		Good
A-OL-10	80	10, P		Good
A-OL-11	75	25, K-B		Good
A-OL-12	80	20, K-B		Good
A-OL-13	85	15, K-B		Good
A-OL-14	85	15, P-C		Good
A-OL-15	80	20, P-C		Good
A-OL-16	90	10, P-C	10, E	Good
A-OL-18	90	7.5, P	2.5, E	Good
A-OL-19	85	10, P	5, E	Good
A-OL-20	85	7.5, P	7.5, E	Good
Blank-1	0	50, P	50, E	Good
Blank-2	0	40, P	60, E	Good

TABLE VIII

TASK II

LIST OF COMPOSITE FILMS
PREPARED BY PROCEDURE B

Film Designation	Matrix	Inorganic Content, %	Organic Binder %, Type	Plasticizer %, Type	Physical Appearance
B-OL-1(F)	F	90	10, P-F		Good
B-OL-2(F)	F	90	10, P-F		Good
B-OL-3(F)	F	90	10, P-F		Good
B-OL-4(N)	N	80	10, P	10, E	Good
B-OL-5(W)	W	80	10, P	10, E	Good
B-OL-6(A)	A	80	10, P	10, E	Good
B-OL-7(PP)	PP	80	10, P	10, E	Good

TABLE IX
TASK II
LIST OF COMPOSITE FILMS
PREPARED BY PROCEDURE D

Film Designation	Inorganic Content, %	Organic Binder %, Type	Plasticizer %, Type	Physical Appearance
D-OL-1	95	5, P		Good
D-OL-2	80	20, P		Good
D-OL-3	85	15, P		Good
D-OL-4	90	10, K-B		Good
D-OL-5	90	10, K-A		Good
D-OL-17	80	10, P	10, E	Good
D-OL-18	90	7.5, P	2.5, E	Good
D-OL-19	85	10, P	5, E	Good

NOTE: For quick reference, the numbers 6 through 16 were not used;

The numbers 17, 18 and 19 correspond to the same formulation as in the films A-OL-17, A-OL-18 and A-OL-19.

4.2.1 Resistivity

This measurement was performed with the equipment described in Appendix A. As indicated above in Section 4.1.2 for the inorganic materials, the samples were vacuum-impregnated with 21% KOH solution by applying a vacuum of 29 inches Hg for 30 minutes. The results obtained are summarized in Tables X and XI.

Measurements are given over longer periods when it was observed that initial readings tended to change with increasing soak time. In all instances, this change was characterized by a decrease in resistivity.

The most noteworthy conclusion that could be reached from these results is that sufficiently low resistance composite separators comprised of the subject materials are attainable. Although some of the composites manifested excessively high resistivities, i. e., A-OL-11, A-OL-12 and A-OL-13, they were subjected to further tests such as dimensional stability and silver and zincate diffusion, etc., in order to facilitate the chemical composition-properties correlation in this phase of the program.

4.2.2 Physical Characteristics and Inertness in KOH

The procedures are similar to those outlined above for the inorganic materials in Section 4.1.1. Three samples were kept immersed in 31% KOH at each temperature. The dry and wet measurements were performed initially and after 7, 15 and 30-day periods. Tables XII and XIII give their physical characteristics.

The results obtained in KOH at 77° and 165°F are summarized in Tables XIV and XV. Considering the results at both temperatures, all of the samples containing Type K binder, manifested evidence of instability. The condition was most severe at 165°F. The samples comprised of Type P organic binder and the B-OL-1(F) and B-OL-2(F), generally manifested less instability than the Type K samples, especially at 165°F. A small amount of flexibilizer E was added in the formulation of the last films to improve their pliability.

Blank runs, made only of binder P and plasticizer E were run under the same conditions and were not adversely affected.

It appeared, therefore, that membranes based on binder P and plasticizer E, particularly the films A-OL-17 and B-OL-6(A) of identical formulation, should be considered good candidates for further study in Task III.

TABLE X

TASK II

COMPOSITE FILMS PREPARED BY PROCEDURE A
RESISTIVITY IN 31% KOH

Binder	Sample Identification	Average of 3 Samples (ohm-cm)
K	A-OL-1	23.0
K	A-OL-2	16.0
K	A-OL-3	31.9
		22.8 (after 1 week in KOH)
		10.8 (after 2 weeks in KOH)
K	A-OL-4	10.3
K	A-OL-5	13.0
P	A-OL-6	15.8
K	A-OL-7	27.1
K	A-OL-8	25.0
P	A-OL-9	486
		419 (after 8 days in KOH)
P	A-OL-10	497 (after 8 days in KOH)
K	A-OL-11	244 (after 15 days in KOH)
K	A-OL-12	212 (after 15 days in KOH)
K	A-OL-13	572
P	A-OL-14	145
		39.8 (after 6 days in KOH)
P	A-OL-15	23.3 (after 6 days in KOH)
P	A-OL-16	29.7 (after 6 days in KOH)
P	A-OL-17	21.4
P	A-OL-18	17.4

TABLE XI

TASK II

COMPOSITE FILMS PREPARED BY PROCEDURE B
RESISTIVITY IN 31% KOH

Binder	Sample Identification	Average of 3 Samples (ohm-cm)
P-F	B-OL-1(F)	19.5
		6.5 (after 45 days in KOH)
P-F	B-OL-2(F)	3.5
P-F	B-OL-3(F)	4.4
P	B-OL-4(N)	13.5

TABLE XII
TASK II
COMPOSITE FILMS: PROCEDURE A
PHYSICAL CHARACTERISTICS-DRY MEASUREMENTS

Binder	Sample Designation	A (cm ²)	t (mils)	m (g)	a _o (%)	p _o (%)
K	A-OL-3	24.0	8	0.45	81.7	64.4
K	A-OL-5	24.7	9	0.80	28.0	40.8
K	A-OL-7	25.8	6	0.60	0.5	0.7
K	A-OL-8	26.0	5	0.50	0.7	1.0
K	A-OL-11	26.0	4	0.41	0.2	0.3
K	A-OL-12	25.8	4	0.32	5.5	6.1
K	A-OL-13	25.6	2	0.17	5.0	6.1
P	A-OL-14	14.4	6	0.37	5.4	9.0
P	A-OL-15	26.2	7	0.71	15.6	23.9
P	A-OL-16	25.0	6	0.65	11.0	18.4
P	A-OL-17	25.6	4	0.42	15.0	24.0
P	A-OL-18	25.8	8	0.89	14.3	24.0
P	A-OL-20	25.9	4	0.20	15.4	24.7

NOTE: A-OL-19 was not tested because it was considered to be in the same category as A-OL-18 and A-OL-20.

TABLE XIII

TASK II

COMPOSITE FILMS: PROCEDURE B
PHYSICAL CHARACTERISTICS - DRY MEASUREMENTS

(All Films Binder P)

Designation	A (cm ²)	t (mils)	m (g)	a _o (%)	p _o (%)
B-OL-1(F)	8.5	12	0.28	68.0	58.4
B-OL-2(F)	Material not dried.				
B-OL-3(F)	20.1	24	1.79	55.4	67.6
B-OL-4(N)	25.9	10	0.62	31.2	29.2
B-OL-5(W)	25.9	6	0.43	21.2	19.6
B-OL-6(A)	25.9	11	0.72	38.9	38.9

TABLE XIV

TASK II

COMPOSITE FILMS PREPARED BY PROCEDURE A
INERTNESS IN 31% KOH
MEASUREMENTS DONE WET

Sample Designation and Binder	Days on Stand	77°F				165°F			
		A (cm ²)	t (mils)	m (g)	P _o (%)	A (cm ²)	t (mils)	m (g)	P _o (%)
A-OL-3 (K)	0	23.7	8	0.72	41.2	25.0	6	0.26	66.7
	7	23.7	8	0.71	40.5	*	*	*	*
	15	23.7	8	0.71	40.0	*	*	*	*
A-OL-5 (K)	0	25.0	9	1.09	41.6	25.0	8	1.02	38.8
	7	25.1	9	1.06	36.4	*	*	*	*
A-OL-7 (K)	0	25.8	6	0.70	20.1	25.6	6	0.73	26.3
	7	25.8	6	0.73	26.0	*	*	*	*
	15	25.8	6	0.72	24.0	*	*	*	*
	30	25.8	6	0.75	29.8	*	*	*	*
A-OL-8 (K)	0	26.1	5	0.64	30.1	25.7	5	0.65	39.6
	7	26.0	5	0.64	31.7	*	*	*	*
	15	26.0	5	0.64	31.4	*	*	*	*
	30	26.0	5	0.64	32.7	*	*	*	*
A-OL-11 (K)	0	25.9	4	0.43	6.2	25.8	4	0.42	7.5
	7	25.9	4	0.44	10.0	25.8	4	0.43	8.9
	15	26.0	4	0.45	11.6	25.7	4	0.42	7.0
	30	26.0	4	0.45	11.5	*	*	*	*
A-OL-12 (K)	0	25.8	4	0.36	14.1	25.8	3	0.34	20.2
	7	25.8	4	0.36	13.1	25.7	3	0.33	19.6
	15	25.8	4	0.37	14.5	*	*	*	*
	30	25.8	4	0.36	12.8	*	*	*	*
A-OL-13 (K)	0	25.8	2	0.20	14.1	25.8	2	0.19	13.8
	7	25.8	2	0.20	18.2	*	*	*	*
	21	*	*	*	*	*	*	*	*
A-OL-14 (P)	0	14.5	6	0.46	31.3	25.7	6	0.78	28.4
	7	14.5	6	0.47	33.5	26.4	6	0.83	37.5
	21	14.6	6	0.48	33.8	27.7	6	0.88	40.4
	30	14.7	6	0.48	33.6	27.9	6	0.90	43.4

(Continued)

TABLE XIV (Continued)

TASK II

COMPOSITE FILMS PREPARED BY PROCEDURE A
INERTNESS IN 31% KOH
MEASUREMENTS DONE WET.

Sample Designation and Binder	Days on Stand	77°F				165°F			
		A ₂ (cm ²)	t (mils)	m (g)	P ₀ (%)	A (cm ²)	t (mils)	m (g)	P ₀ (%)
A-OL-15 (P)	0	26.4	7	0.91	32.3	26.3	6	0.85	35.3
	7	26.8	7	0.92	34.9	26.5	6	0.86	37.1
	15	26.9	7	0.93	35.2	27.0	6	0.87	39.0
	30	*	*	*	*	*	*	*	*
A-OL-16 (P)	0	25.4	6	0.75	19.8	26.1	7	0.85	19.6
	7	25.7	6	0.75	19.8	27.4	7	0.91	30.8
	15	26.0	6	0.77	22.3	31.2	7	1.00	40.0
	30	25.9	6	0.76	20.7	32.6	7	1.07	48.3
A-OL-17 (P)	0	26.0	5	0.69	26.8	26.1	5	0.69	29.9
	0	26.0	5	0.69	26.7	25.8	5	0.69	32.4
	15	26.0	5	0.69	27.4	25.8	5	0.71	32.5
	30	26.0	5	0.69	26.3	26.3	5	0.69	32.5
A-OL-18 (P)	0	25.9	8	1.07	27.1	25.3	8	1.07	28.3
	7	25.9	8	1.08	27.9	25.3	8	1.11	34.0
	15	26.0	8	1.07	27.3	25.4	8	1.11	33.4
	30	26.0	8	1.08	28.4	25.5	8	1.11	33.0
A-OL-20 (P)	0	25.8	4	0.52	27.6	25.7	4	0.52	27.6
	7	25.5	4	0.52	29.6	25.2	4	0.51	26.4
	15	25.5	4	0.52	28.8	25.2	4	0.52	26.7
	30	25.5	4	0.52	28.2	25.2	4	0.53	29.7
Blank-1 (P)	0	25.9	2	0.11	—	25.9	1	0.09	—
	7	25.4	2	0.13	—	23.9	1	0.09	—
	15	25.3	2	0.12	—	23.8	1	0.09	—
	30	25.3	2	0.14	—	23.7	1	0.09	—
Blank-2 (P)	0					26.1	2	0.13	—
	7					24.7	2	0.13	—
	15					24.4	2	0.13	—
	30					24.3	2	0.12	—

NOTE: A-OL-19 was not tested because it was considered to be in the same category as A-OL-18 and A-OL-20.

* Test discontinued: sample not suitable for further testing.

TABLE XV
TASK II
COMPOSITE FILMS PREPARED BY PROCEDURE B
INERTNESS IN 31% KOH
MEASUREMENTS DONE WET
(All Films Binder P)

Sample Designation	Days on Stand	77°F				165°F			
		A ₂ (cm ²)	t (mils)	m (g)	Po (%)	A ₂ (cm ²)	t (mils)	m (g)	Po (%)
B-OL-1(F)	0	8.6	11	0.35	24.0	18.4	11	0.83	24.3
	7	8.3	11	0.36	25.7	18.1	11	0.85	27.2
	15	8.4	11	0.36	27.1	18.2	11	0.86	30.8
	30	8.5	11	0.36	25.6	17.7	11	0.84	27.5
B-OL-2(F)	0	24.7	28	4.18	*	24.8	29	4.74	*
	7	24.9	28	4.14	*	23.8	29	4.40	*
	15	24.4	27	4.00	*	22.4	28	4.22	*
	30	24.4	26	4.12	*	19.7	28	4.36	*
B-OL-3(F)	0	24.1	24	2.94	60.1	23.8	24	2.91	64.1
	7	19.9	24	2.20	26.2	19.2	24	2.40	46.0
	15	19.9	24	2.21	26.3	19.1	24	2.46	50.8
	30	19.9	24	2.22	27.5	19.1	24	2.51	53.2
B-OL-4(N)	0	25.9	10	0.86	28.4	25.8	9	0.73	30.6
	7	25.9	10	0.87	30.3	26.1	9	0.74	31.3
	15	25.9	10	0.87	27.3	26.2	9	0.76	30.3
	30	26.0	10	0.87	26.8	26.3	9	0.75	29.5
B-OL-5(W)	0	25.8	7	0.52	22.0	25.7	7	0.60	23.2
	7	25.6	7	0.53	23.8	25.2	7	0.62	26.7
	15	25.6	7	0.53	23.6	25.3	7	0.62	26.6
	30	25.6	7	0.52	21.6	25.3	7	0.63	27.5
B-OL-6(A)	0	25.7	12	1.30	56.5	25.6	13	1.34	50.2
	7	25.6	13	1.29	51.9	25.5	14	1.36	49.2
	15	25.6	13	1.22	45.4	25.5	14	1.38	51.1
	30	25.6	13	1.23	46.2	25.6	13	1.36	51.1

* Not measured (samples were not originally dried).

4.2.3 Impermeability to Ions

These tests were performed concurrently with the dimensional stability tests. The procedures are given in Appendix A. The results obtained for films prepared by Procedures A and B are summarized in Tables XVI and XVII.

For Procedure D (dip coated electrodes), uncharged silver plates were used, of the following specifications:

Dimensions:	1.6" x 1.6" x 0.022"
Silver powder:	4.5 grams
Approximate nominal capacity at high rate:	1 Ah

After the dip-coating procedure was completed, the coated electrode was charged at 75 mA for 20 hours. Then, the coated electrode was thoroughly rinsed in distilled water and immersed in a polysulfone case and covered with 50 ml of 31% KOH solution. One-ml samples of solution were removed from the solution and analyzed for silver by the colorimetric procedure given in Appendix A. The diffusion rates were calculated ordinarily for a period of six hours of operating time, unless the diffusion rates were extremely low, whereupon a longer period was necessary. The silver diffusion rates are listed in Table XVIII.

The D-OL-4 and D-OL-5 formulations are essentially the same as that for the A-OL-7 and A-OL-8 films, respectively. The diffusion rate for the D-OL-4 film appears to be less than that of the A-OL-7 film. For the D-OL-5 film, the rate must be considered as equal to or less than the A-OL-8 films. The low diffusion rates manifested by the D-OL-1 and D-OL-2 films indicated that further study of films based on P-type organic binder prepared by this procedure was in order under Task III.

4.2.4 Resistance to Oxidation

Tables XIX and XX give all data on films prepared by procedures A and B. Procedure D (dip coated electrodes) can be qualitatively evaluated in cell tests by the OCV retention capability on stand.

4.2.5 Discussion of Results

The results listed in Tables XVI, XVII, and XVIII indicate that silver diffusion rates of composite films are significantly lower than those obtained for the 100% inorganic samples as listed in Table V. No conclusions can be reached about the comparison of zinc diffusion rates; generally, these rates are about the same for both types of material, although occasionally the values for the composite films are lower.

TABLE XVI

TASK II
COMPOSITE FILMS (PROCEDURE A)
IMPERMEABILITY TO IONS

Sample Designation and Binder	Silver Diffusion, a (mg-mil/in ² -hr.)		Zincate Diffusion, * (moles-mil/in ² -min)	
	Readings	Average	Readings	Average
A-OL-3 (K)	0.119 0.203	0.161	NOT TESTED ⁽¹⁾	
A-OL-4 (K)	NOT TESTED ⁽¹⁾		16.0	16.0
A-OL-7 (K)	0.144 0.072 0.072	0.096	6.02 4.80 2.33	4.38
A-OL-8 (K)	0.117 0.023 0.047 0.093 0.056	0.067	8.06 3.11 5.86 8.84	6.47
A-OL-9 (P)	NOT TESTED ⁽²⁾		0.53 0.94 0.16 0.14	0.44
A-OL-10 (P)	NOT TESTED ⁽²⁾		0.34 0.23 0.18 0.20 0.46	0.28
A-OL-11 (K)	0.020 0.094 0.094 0.019 0.094	0.064	0.15 0.38 0.29 0.44 0.29	0.31
A-OL-12 (K)	trace	trace	1.50 1.30 1.27 1.20 1.19	1.29

(1) Materials found not suitable for further testing.

(2) Tests eliminated because of high resistivity.

* Zincate diffusion rate = $b \times 10^{-5}$, reported as \underline{b} . (Continued)

TABLE XVI (Continued)

TASK II

COMPOSITE FILMS (PROCEDURE A)
IMPERMEABILITY TO IONS

Sample Designation and Binder	Silver Diffusion, a (mg-mil/in ² -hr.)		Zincate Diffusion, * (moles-mil/in ² -min)	
	Readings	Average	Readings	Average
A-OL-13 (K)	trace 0.004 0.007 0.070	0.020	0.91 0.18 0.36 0.35 0.46	0.45
A-OL-14 (P)	0.028 0.028 0.023	0.028	0.61 0.35 0.61	0.52
A-OL-15 (P)	trace	trace	2.11 2.34 2.05 1.47	1.99
A-OL-16 (P)	NOT TESTED(1)		NOT TESTED(1)	
A-OL-17 (P)	0.141 0.085 0.057	0.094	2.43 2.12 2.39	2.31

(1) Materials found not suitable for further testing.

* Zincate diffusion rate = $b \times 10^{-5}$, reported as b.

TABLE XVII

TASK II

COMPOSITE FILMS (PROCEDURE B)
IMPERMEABILITY TO IONS

(All Films Binder P)

Sample Designation	Silver Diffusion, a (mg-mil/in ² -hr.)		Zincate Diffusion, * (moles-mil/in ² -min)	
	Readings	Average	Readings	Average
B-OL-2(F)	0.160	0.160	NOT TESTED ⁽¹⁾	
B-OL-3(F)	0.138	0.124	5.4	6.40
	0.125		4.8	
	0.085		7.4	
	0.098		8.3	
	0.175		6.1	
B-OL-4(N)	0.274	0.287	8.08	7.48
	0.300		7.30	
			7.06	

(1) Material found not suitable for further testing.

* Zincate diffusion rate = $b \times 10^{-5}$, reported as b.

TABLE XVIII

TASK II

COMPOSITE FILMS: PROCEDURE D
SILVER DIFFUSION

Sample Designation and Binder	Silver Diffusion, a (mg-mil/in ² -hour)		Comments
	Readings	Average	
D-OL-1 (P)	<u>6-hr period</u> 0.006 0.023 0.028 0.011 0.011	0.016	
D-OL-2 (P)	<u>26.5-hr period</u> 0.008 0.008 0.005 0.005 0.008	0.007	Longer time span for measurement required because of low diffusion rate.
D-OL-3 (P)	<u>2-hr period</u> 0.034 0.085 0.137 0.137		Relatively high rate, could be due to openings at edges.
D-OL-4 (K)	<u>69.5-hr period</u> 0.007 0.005 0.013 0.007 0.003	0.007	Longer time span for measurement required because of low diffusion rate.
D-OL-5 (K)	<u>6-hr period</u> 0.143 trace trace		Lack of uniformity; could be due to openings at edges.

TABLE XIX

TASK II
COMPOSITE FILMS PREPARED BY PROCEDURE A
RESISTANCE TO OXIDATION

Binder	Sample Designation	Days on Stand	Silver Pick-up, \bar{c} (mg/cm ²)			
			77°F		165°F	
			Readings	Average	Readings	Average
K	A-OL-3	1	7.0	7.0	20.15	20.15
		2	14.0	14.0	44.0	44.0
K	A-OL-4	1			29.65	29.65
		4	4.77	4.77		
K	A-OL-7	7	5.30 5.30 5.30	5.30	5.30 5.30 5.30	5.30
		15	7.42 5.30	6.71	*	
		30	*		*	
K	A-OL-8	7	3.71 4.61 3.71	3.86	*	
		15	*		*	
P	A-OL-9	7	0 0 0	0	9.54 8.48 8.48	8.83
		15	1.06 1.06 1.06	1.06	13.78 13.78 11.66	13.07
		30	1.06 2.12 2.12	1.77	13.78 13.78 13.78	13.78
P	A-OL-10	7	2.12 2.12 2.12	2.12	13.78 14.84 14.84	14.49
		15	5.30 5.30 3.18	4.59	12.72 12.78 12.72	13.07

(Continued)

TABLE XIX (Continued)

TASK II
COMPOSITE FILMS PREPARED BY PROCEDURE A
RESISTANCE TO OXIDATION

Binder	Sample Designation	Days on Stand	Silver Pick-up, $\frac{c}{(mg/cm^2)}$			
			77°F		165°F	
			Readings	Average	Readings	Average
P	A-OL-10 (cont'd)	30	12.72 5.30 11.66	9.89	15.90 16.96 13.78	15.55
K	A-OL-11	7	3.18 3.18 3.18	3.18	10.60 10.60 12.72	11.31
		15	8.48 9.54 7.42	8.48	13.78 12.72 *	13.25
		30	14.84 14.84 15.90	15.19	12.72 14.84 *	13.78
K	A-OL-12	7	3.18 3.18 3.18	3.18	*	
		15	7.42 8.48 7.42	7.77	*	
		30	14.84 12.72 14.84	14.13	*	
K	A-OL-13	7	2.12 3.18 3.18	2.83	*	
		15	4.24 4.24 4.24	4.24	*	
		30	*		*	

(Continued)

TABLE XIX (Continued)

TASK II
COMPOSITE FILMS PREPARED BY PROCEDURE A
RESISTANCE TO OXIDATION

Binder	Sample Designation	Days on Stand	Silver Pick-up, \bar{c} (mg/cm ²)			
			77°F		165°F	
			Readings	Average	Readings	Average
P	A-OL-14	7	6.36	6.89	28.62	27.56
			7.42		26.50	
		15	11.66	12.19	23.32	23.32
			12.72		23.32	
		30	20.14	19.61	21.20	21.20
			19.08		21.20	
P	A-OL-15	7	13.78	13.78	36.04	36.04
			13.78		36.04	
		15	19.08	19.08	40.28	39.75
			19.08		39.22	
		30	23.82	22.79	30.74	32.33
			22.26		33.92	
P	A-OL-16	7	3.18	3.18	23.32	28.09
			3.18		32.86	
		15	4.24	4.51	20.14	23.32
			4.77		26.50	
		30	8.48	8.48	21.20	24.38
			8.48		27.56	
P	A-OL-17	7	0.54	0.43	9.67	8.57
			0.38		7.83	
			0.38		8.21	
		15	0.76	0.81	7.45	7.97
			0.81		8.48	
			0.86		7.99	
		30	1.52	1.41	9.99	9.83
			1.40		9.40	
			1.30		10.10	

* Samples could not be handled

TABLE XX

TASK II

COMPOSITE FILMS PREPARED BY PROCEDURE B
(ALL BINDER P)
RESISTANCE TO OXIDATION

Sample Designation	Days on Stand	Silver Pick-up, \bar{c} (mg/in ²)			
		77°F		165°F	
		Readings	Average	Readings	Average
B-OL-2(F)	21	3.18 2.65	2.92	5.30 5.30	5.30
	28	4.24 3.71	3.98	7.42 7.42	7.42
	35	4.24 4.24	4.24	4.24 4.24	4.24
B-OL-3(F)	7	trace trace trace	trace	2.12 2.12 2.12	2.12
	15	1.06 1.06 1.06	1.06	2.12 3.18 3.18	2.83
	30	1.59 1.06 1.06	1.24	3.71 3.71 4.24	3.89
B-OL-4(N)	7	trace trace trace	trace	2.12 4.24 3.18	3.18
	15	trace trace 0.53	0.18	1.06 4.24 5.83	3.71
	30	0.27 0.38 0.32	0.32	*	

* Solution gelled - Not Measured.

However, the resistance to silver oxidation is higher for the composite film.

The relative orders of silver diffusion rates and silver oxidation rates indicate that silver ions pass through the inorganic materials without any reaction. On the other hand, the composite films could be impeding the passage of silver ions by reduction of the silver. This is evidenced by discoloration of the composite separator during the silver diffusion test.

Referring to Table XVI and XVII, it appears that the nature of the organic binder itself does not affect the silver or zincate diffusion rates. Since both types of experiments were performed over relatively short periods of time in 31% KOH solution at 77°F, the instability of the Type K component would not be revealed. However, the resistance-to-oxidation test showed that type P materials survived longer than the Type K materials at 165°F (Table XIX).

4.2.6 Comments and Conclusions

From all of the studies conducted under Task II, including both formulation and evaluation, it was quite evident that composite films of at least 80% inorganic material 3420-09 could be prepared with promising properties. During the early preparative efforts involving Type K organic binder, it was not certain whether the lack of stability in 31% KOH was due to the procedure itself, or to the binder. Actually, prior studies of the Type K binder itself had indicated greater stability in KOH solution at elevated temperatures. This was the reason for its selection in this investigation, initially. However, it was recognized that the specific Type K materials evaluated up to that point were in a highly oriented polymeric state. It was not known to what extent the morphological character of Type K binder contributed to such stability.

By the end of Task II, enough composite films had been prepared with Type K binder to indicate that it would not be sufficiently stable in 31% KOH solution at 165°F because of the nature of its morphological state under the preparative conditions involved. Correspondingly, Type P organic binder appears to be far more stable, regardless of its morphology and must be considered the candidate for further studies under Task III. However, further improvements in fabrication procedures may be required. This would include relatively small amounts of plasticizer.

The composite formulation used in the last two films (A-OL-17 and A-OL-18) appeared to be the point of convergence of the series of mixes. This formulation (80% inorganic, 10% binder P, 10% plasticizer E) referred to as 80/10/10 in short was extensively evaluated on Task III on cast films (Procedure A), films supported by a porous matrix (Procedure B) and films deposited directly on electrodes by dip coating (Procedure D).

4.3 TASK III: FINAL FILM EVALUATION

All the results of the exploratory program pointed to the adoption of the composite film system based on type 3420-09 inorganic material, binder P and plasticizer E and prepared by Procedures A, B or D.

Slight variations in the relative amounts of the components were studied through the films made by Procedure A, although at an early stage, it was decided to select for cell testing one single formulation, but applied by the three procedures.

The selected formulation was 80/10/10 (as explained in Paragraph 4.2.6) and was extensively evaluated. In all the following tests, there is a general table of data for all films, a detailed table of data for the various batches of the same selected film and, when applicable, a table of the validity range of the data.

4.3.1 Resistivity

Tables XXI and XXIV give the general data for all films made by Procedure A and Procedure B, respectively.

Tables XXII, XXIII, XXV, and XXVI give the details and analysis of the selected membranes.

The cast film, A-OL-17, averages about 16 ohm-cm and the film deposited on the matrix 12.2 ohm-cm. Considering that the method error is about 10%, the mean deviation was found to be within the error limits for all batches, which showed relatively good membrane uniformity, and even for the grand average between the batches, which showed relatively good fabrication reproducibility.

4.3.2 Silver Diffusion

This investigation was carried out on the best films at 77°F and 165°F. The data are presented in specific rates (mg-mil/in²-hr) and in absolute rates (mg/in²-hr) which are more representative of the intrinsic value of the membrane.

The various films studied are reported in Table XXVII for Procedure A and Table XXXI for Procedure B.

The selected formulation is reported in detail in other tables. For Procedure A, the selected film A-OL-17 is reported in detail in Tables XXVIII, XXIX, and XXX. For Procedure B, the selected film B-OL-6(A) is reported in detail in Tables XXXII, XXXIII, and XXXIV.

The method error is the sum of the errors accumulated during the experimental analytical procedure. Three liquid samples are taken

TABLE XXI

TASK III

COMPOSITE FILMS (PROCEDURE A)
RESISTIVITY IN 31% KOH AT 77°F

Sample Designation	Thickness (mils)	Average of 3 Samples (Ω -cm)		Area Resistance of One Layer ($m\Omega$ -in ²)
		Initial	After 1 Day	
A-OL-17	3	24.4	16.0	19.0
A-OL-18	8	14.8		46.6
A-OL-19	4.5	18.0	16.5	31.9
A-OL-20	3	11.5		13.6

NOTE: A-OL-17 is the average of several batches (see Tables XXV and XXVI for detailed data and analysis).

TABLE XXII

TASK III

COMPOSITE FILMS (PROCEDURE A)
A-OL-17 SERIES RESISTIVITY IN 31% KOH AT 77°F

Batch Number	Curing Temp. (°F)	Thickness (mils)	Average of 3 Samples After Soaking (Ω -cm)			Area Resistance of 1 Layer ($m\Omega$ -in ²)	
			Initial	1 day	8 days		
A-OL-17-1	250	5	21.4		7.8		
A-OL-17-2	350	2	17.4			13.7	
A-OL-17-3	150	3	23.4		18.8	22.2	Rejected from further analysis because Procedure was not firmed up yet.
A-OL-17-4	150	3	23.8	17.0		20.1	
A-OL-17-5	150	3	27.5	15.9		18.8	
A-OL-17-6	150	3	23.1	15.2		18.0	Procedure firmed up, Films acceptable.
Average		3	24.4	16.0		19.0	

TABLE XXIII

TASK III

COMPOSITE FILMS (PROCEDURE A) (A-OL-17 SERIES)
RESISTIVITY IN 31% KOH AT 77°F. RANGE OF VALIDITY

Material Designation	Sample			Batch		Mean Deviation	Formulation		
	Sample Number	Thickness (mils)	Readings (Ω -cm)	Average (Ω -cm)	Method Error ($\epsilon=10\%$)		Average (Ω -cm)	Total Error	Mean Deviation
A-OL-17-4	1	3	23.8	23.8	± 2.4	1.43			
	2	3	26.0						
	3	3	21.7						
A-OL-17-5	1	3	28.2	27.5	± 2.8	0.97	24.8	± 2.5	1.80
	2	3	28.2						
	3	3	26.0						
A-OL-17-6	1	3	26.0	23.1	± 2.3	1.90			
	2	3	21.7						
	3	3	21.7						

TABLE XXIV

TASK III

COMPOSITE FILMS (PROCEDURE B)
RESISTIVITY IN 31% KOH AT 77°F

Sample Designation	Thickness (mils)	Average of 3 Samples (Ω -cm)	Area Resistance of 1 Layer ($m\Omega$ -in ²)
B-OL-5(W)	7.5	37.1	109
B-OL-6(A)	14.3	12.2	68.8
B-OL-7(PP)	10.5	61.4	253.8

NOTE: B-OL-6(A) is the average of several batches (see Tables XXVIII and XXIX for detailed data and analysis).

TABLE XXV

TASK III

(PROCEDURE B) B-OL-6(A) SERIES
RESISTIVITY IN 31% KOH AT 77°F

Batch Designation	Thickness (mils)	Average of 3 Samples (Ω -cm)	Area Resistance of 1 Layer ($m\Omega$ -in ²)
B-OL-6(A)-1	11	12.2	52.8
B-OL-6(A)-2	16	12.2	76.8
B-OL-6(A)-3	16	12.2	76.8
Average	14.3	12.2	68.8

TABLE XXVI

TASK III

COMPOSITE FILMS: (PROCEDURE B) B-OL-6(A) SERIES
RESISTIVITY IN 31% KOH AT 77°F
RANGE OF VALIDITY

Batch Designation	Sample			Batch			Formulation		
	Sample Number	Thickness (mils)	Readings (Ω - cm)	Average (Ω - cm)	Method Error ($\epsilon = 10\%$)	Mean Deviation	Average (Ω - cm)	Total Error	Mean Deviation
B-OL-6(A)-1	1	11.1	12.3	12.2	± 1.2	0.30	12.2	± 1.2	0.0
	2	11.0	11.8						
	3	10.8	12.6						
B-OL-6(A)-2	1	16.0	11.4	12.2	± 1.2	0.53	12.2	± 1.2	0.0
	2	16.0	13.0						
	3	16.0	12.2						
B-OL-6(A)-3	1	16.0	11.4	12.2	± 1.2	0.80	12.2	± 1.2	0.0
	2	16.0	13.4						
	3	16.0	11.8						

TABLE XXVII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A
A-OL SERIES SILVER DIFFUSION(Specific mg-mil/in²-hr; Absolute mg/in²-hr.)

Sample Designation	Composition			Nominal Thickness (Mils)	77°F			165°F		
					Specific Readings	Average		Specific Readings	Average	
	% Inorganic	% Organic Binder	% Plasticizer			Specific	Absolute		Specific	Absolute
							Absolute			Absolute
A-OL-17	80	10 P	10 E	—	—	0.081	0.030	—	0.218	0.083
A-OL-18	90	7.5P	2.5E	3	0.032			0.115		
					0.032			0.136		0.042
					0.032	0.032	0.010			
A-OL-20	85	7.5P	7.5E	3	0.104			0.147		0.049
					0.099	0.102	0.034	0.147	0.049	

NOTE: A-OL-17 is the average of several batches (see Tables XXVIII, XXIX, and XXX for detailed data and analysis).

TABLE XXVIII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A
A-OL-17 SERIES SILVER DIFFUSION SUMMARY

SPECIFIC = mg-mil/in²-hr; ABSOLUTE = mg/in²-hr

Sample Designation	77°F		165°F	
	Average		Average	
	Specific	Absolute	Specific	Absolute
A-OL-17-4	0.095	0.032	0.192	0.064
A-OL-17-5	0.089	0.036	0.246	0.098
A-OL-17-6	0.058	0.023	0.215	0.086
Average	0.081	0.030	0.218	0.083

TABLE XXIX

TASK III

COMPOSITE FILMS (PROCEDURE A)
SILVER DIFFUSION AT 77°F FOR DIFFERENT
BATCHES OF SELECTED FILM
(mg-mil/in²-hr.)

Batch Code	Sample				Batch		Formulation	
	Physical Sample No.	Avg. for Liquid Samples	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation	Average	Mean Deviation
A-OL-17-4	1	0.162	0.141	0.016	0.095	0.031		
		0.145						
		0.117						
	2	0.095	0.086	0.006				
		0.084						
		0.079						
	3	0.065	0.058	0.005				
		0.050						
		0.058						
A-OL-17-5	1	0.098	0.097	0.006	0.089	0.005		
		0.089						
		0.105						
	2	0.095	0.086	0.006				
		0.082						
		0.080						
	3	0.088	0.085	0.005				
		0.078						
		0.089						
A-OL-17-6	1	0.049	0.051	0.005	0.058	0.005	0.081	0.015
		0.058						
		0.045						
	2	0.060	0.059	0.004				
		0.063						
		0.053						
	3	0.066	0.065	0.002				
		0.067						
		0.061						

TABLE XXX

TASK III

COMPOSITE FILMS (PROCEDURE A)
SILVER DIFFUSION AT 165°F FOR DIFFERENT
BATCHES OF SELECTED FILM
(mg-mil/in²-hr.)

Batch Code	Sample			Batch		Formulation	
	Physical Sample No.	Avg. for Liquid Samples	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation	Average
A-OL-17-4	1	0.196					
		0.183					
		0.186	0.188	0.005			
A-OL-17-5	2	0.197					
		0.196					
		0.193	0.195	0.002	0.192	0.004	
	1	0.265					
		0.246					
A-OL-17-6		0.278	0.263	0.011			
	2	0.233					
		0.227					
		0.227	0.229	0.003	0.246	0.017	
	1	0.194					
		0.201					
		0.188	0.194	0.004			
	2	0.233					
		0.240					
		0.233	0.235	0.003	0.215	0.021	0.218
							0.019

TABLE XXXI

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE B
B-OL SERIES SILVER DIFFUSION(Specific = mg-mil/in²-hr; Absolute = mg/in²-hr.)

Sample Designation	Composition			Nominal Thickness (Mils)	77°F			165°F		
					Specific Readings	Average		Specific Readings	Average	
	% Inorganic	% Organic Binder	% Plasticizer			Specific	Absolute		Specific	Absolute
B-OL-5(W)	80	10P	10E	7	0.025 0.016	0.020	0.003	0.046 0.042	0.044	0.006
B-OL-6(A)	80	10P	10E	13	—	0.026	0.002	—	0.051	0.004
B-OL-7(PP)	80	10F	10E	10	0.011 0.012 0.013	0.012	0.001	0.022 0.036	0.029	0.003

NOTE: B-OL-6(A) is the average of several batches (see Tables XXXII, XXXIII, and XXXIV for detailed data and analysis).

TABLE XXXII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE B
B-OL-6(A) SERIES SILVER DIFFUSION SUMMARY

(Specific = mg-mil/in²-hr; Absolute = mg/in²-hr.)

Sample Designation	77°F		165°F	
	Average		Average	
	Specific	Absolute	Specific	Absolute
B-OL-6(A)-1	0.032	0.003	0.056	0.005
B-OL-6(A)-2	0.023	0.001	0.039	0.002
B-OL-6(A)-3	0.022	0.001	0.059	0.004
Average	0.026	0.002	0.051	0.004

TABLE XXXIII

TASK III

COMPOSITE FILMS (PROCEDURE B)
SILVER DIFFUSION AT 77°F FOR DIFFERENT
BATCHES OF SELECTED FILM
(mg-mil/in²-hr.)

Batch Code	Sample				Batch		Formulation	
	Physical Sample Number	Avg. for Liquid Samples	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation	Average	Mean Deviation
B-OL-6(A)-1	1	0.012 0.027	0.020	0.008	0.032	0.012		
	2	0.045 0.042	0.044	0.002				
B-OL-6(A)-2	1	0.017 0.017 0.037	0.024	0.009	0.023	0.004		
	2	0.012 0.046	0.029	0.017				
	3	0.017 0.017	0.017	0.000				
	1	0.012 0.017	0.015	0.003				
	2	0.017 0.021	0.019	0.002				
B-OL-6(A)-3	3	0.037 0.025	0.031	0.006	0.022	0.006	0.026	0.004

TABLE XXXIV

TASK III

COMPOSITE FILMS (PROCEDURE B)
SILVER DIFFUSION AT 165°F FOR DIFFERENT
BATCHES OF SELECTED FILM
(mg-mil/in²-hr.)

Batch Code	Sample				Batch		Formulation	
	Physical Sample Number	Avg. for Liquid Samples	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation	Average	Mean Deviation
B-OL-6(A)-1	1	0.089	0.058					
	2	0.027	0.058	0.031				
B-OL-6(A)-2		0.072						
		0.033	0.053	0.020	0.056	0.003		
	1	0.037						
		0.046						
B-OL-6(A)-3		0.029	0.037	0.006				
	2	0.037						
		0.041						
		0.046	0.041	0.003	0.039	0.002		
	1	0.066						
		0.050	0.058	0.008				
		0.066						
	2	0.054	0.060	0.006	0.059	0.001	0.051	0.008

from the secondary compartment of the diffusion apparatus after the requisite time for silver diffusion through the membrane under test. Each sample measuring 1 cm³ (with an error less than 5%) is placed in a colorimeter after adding reagents. Three readings are taken on the colorimeter for each sample, which goes through the colorimeter three times. The random (or systematic) error due to the compounded colorimeter measurements was found to be less than 8%. The total error on one physical sample is a maximum of 13%. It can be seen that the mean deviation on the physical samples is very often within the error limits, and sometimes as low as 5%.

However, the error between different batches of the same film is greater and may be 15% because of slight variations in thickness between films. Even so, the mean deviation between batches is within the error limits, although very close.

A very interesting study was performed on the membrane tested for silver diffusion. After removal from the diffusion apparatus, the membrane was analyzed for silver pick-up. Table XXXV shows that the silver pick-up is very small, even at 165°F.

At one time during the program, the silver diffusion rates for dip-coated electrodes were compared with some data obtained by the diffusion apparatus for equivalent formulations. In order to attempt a correlation between the two methods, a third method for performing this measurement was initiated. This consisted of wrapping one layer of composite film around a charged silver electrode. This electrode had the same specifications (dimensions, weight and charge) as given above for Procedure D film evaluations (Paragraph 4.2.3). After the charging was completed, the electrode was thoroughly rinsed with distilled water and dried at 65°C for two hours. After the composite film separator was wrapped around the electrode, the assembly was placed in a case and immersed in 31% KOH solution. The procedures for measuring silver diffusion rates were as described for the dip-coated electrodes. The data presented in Table XXXVI showed a close equivalence at 77°F for the selected formulation 80/10/10 used in films A-OL-17 and D-OL-17.

In summary, the results obtained show that the silver diffusion rates for the composite films are lower than those for inorganic separators. It is to be noted from the tests at 165°F that there was an increase in the silver diffusion rate to about the level of that noted at 77°F for the inorganic separators. This is still a relatively low rate, since inorganic separators by themselves perform well in secondary cells over significant periods of time at temperatures as high as 212°F.*

* op. cit. Arrance, F. C.

TABLE XXXV

TASK III

COMPOSITE SEPARATORS: PROCEDURES A AND B WITH 80-10-10 FORMULATION
 SILVER PICK-UP AFTER SILVER DIFFUSION
 (Absolute = mg/in²) (Specific = mg/in²-mil)

Batch Designation	77°F						165°F					
	Batch			Formulation			Batch			Formulation		
	Absolute		Average	Specific		Average	Absolute		Average	Specific		Average
	Readings			Average			Readings			Average		
A-OL-17-4 (3 mils)	trace						trace					
	trace		trace				0.12		0.06		0.02	
	trace											
A-OL-17-5 (3 mils)	trace											
	trace		trace		trace	trace	0.11		0.11		0.04	
	trace											0.03
A-OL-17-6 (3 mils)	trace											
	trace		trace				0.08		0.08		0.03	
	trace											
B-OL-6(A)-1	*						*					
B-OL-6(A)-2 (10 mils)	1.37						3.08					
	0.64	1.01	0.06		0.76	0.05	3.02	3.05		0.19		2.48
B-OL-6(A)-3 (16 mils)	0.67						2.04					
	0.46	0.52	0.03				1.80	1.92		0.12		
	0.43											0.16

* B-OL-6(A)-1 was not tested.

TABLE XXXVI

TASK III

COMPARISON OF SILVER DIFFUSION RATES
OF COMPOSITE SEPARATORS BY 3 DIFFERENT METHODS
(mg-mil/hr-in²) (AVERAGE OF AT LEAST 3 READINGS)

Film Designation	Diffusion Apparatus	Wrapped Electrodes	Dip Coated Electrodes		
	77°F	77°F	Corresponding Film Designation	77°F	165°F
—	—	—	D-OL-1	0.016	0.117
A-OL-7	0.090	0.005	D-OL-4	0.007	—
A-OL-8	0.068	—	D-OL-5	0.090	—
A-OL-17-1	0.040	0.022	D-OL-17	0.048	0.132
A-OL-18	0.032	0.150	D-OL-18	0.085	0.136
B-OL-3(F)	0.124	0.188			

4.3.3 Zincate Diffusion

The investigation was carried out on the best films, and general data are presented in Table XXXVII for Procedure A and Table XLI for Procedure B.

The selected formulation was tested on different batches of A-OL-17 and B-OL-6(A). Details and analysis are reported in Tables XXXVIII, XXXIX, and XL for Procedure A and XLII, XLIII, and XLIV for Procedure B.

The method error was found to be in the range of 15%. The mean deviation is usually within the error limits.

The zincate diffusion rates of the composite films are generally the same as those for the inorganic separators. It is of interest to note that the zincate diffusion rates do not appear to change with increasing temperature.

4.3.4 Resistance to Silver Oxidation

Here again, the data for silver pick-up were presented in absolute values (mg/in^2) and in specific values ($\text{mg}/\text{in}^2\text{-mil}$) as it became apparent that comparison between membranes made by different procedures A and B would be difficult since the B series are usually made on relatively thick matrices. Various films of Procedure A are reported in Table XLV. Various films of Procedure B are reported in Table XLVIII. Details and analysis are reported in Tables XLVI, XLVII, XLIX and L.

The results of the silver oxidation tests indicate that the plasticizer E (blank runs) must not be contributing to instability.

4.3.5 Comments and Conclusions

Task III concentrated on the full characterization of one selected formulation, 80/10/10, applied by three different procedures on repeated batches of cast film (A-OL-17) or film deposited on matrix (B-OL-6(A)). Results of resistivity, silver diffusion, zincate diffusion and resistance to silver oxidation show general uniformity of membrane and reproducibility of fabrication. It appears that the values obtained were sufficiently encouraging to warrant cell testing for Task IV, in the last three months of the program.

It is important to note that one separator of the B-OL series is markedly superior for silver diffusion and zincate diffusion. The B-OL-7(PP), consisting of the same formulation 80/10/10 applied on a new matrix PP, was evaluated at the end of the program and only limited cell tests were performed.

TABLE XXXVII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A

A-OL SERIES ZINC DIFFUSION

SPECIFIC = moles·mi/in²·min^{*}; ABSOLUTE = moles/in²·min. *

Sample Designation	Composition			Nominal Thickness (mils)	77°F			165°F				
					b	Average		b	Average			
	% Inorganic	% Organic Binder	% Plasticizer			Specific Readings	Specific		Absolute	Specific Readings	Specific	Absolute
A-OL-17	80	10	P	10	E	—	—	1.55	0.57	—	1.79	0.63
A-OL-18	90	7.5	P	2.5	E	3	2.15			2.12		0.71
							1.76					
							2.28					
							2.58					
						—	2.04	2.16	0.72			
A-OL-19	85	10	P	5	E	NOT TESTED						
A-OL-20	85	7.5	P	7.5	E	3	4.40		1.31	4.23	3.91	1.30
							3.48					

* Zinc diffusion rate = $b \times 10^{-5}$, reported as \bar{b} .

NOTE: A-OL-17 is the average of several batches (see Tables XXXVIII, XXXIX, and XL for detailed data and analysis).

TABLE XXXVIII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A
A-OL-17 SERIES ZINC DIFFUSION SUMMARY

Specific: moles-mil/in²-min.*; Absolute: moles/in²-min.*

Designation	77°F		165°F	
	<u>b</u> Average		<u>b</u> Average	
	Specific	Absolute	Specific	Absolute
A-OL-17-4	2.31	0.77	2.67	0.89
A-OL-17-5	1.14	0.46	1.45	0.58
A-OL-17-6	1.20	0.48	1.26	0.42
Average	1.55	0.57	1.79	0.63

*Zinc Diffusion Rate = $\underline{b} \times 10^{-5}$, reported as b.

TABLE XXXIX

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A
 ZINC DIFFUSION AT 77°F FOR
 DIFFERENT BATCHES OF SELECTED FILM

(moles -mil/in²-min)*

Membrane Code	Sample		Batch		Formulation	
	Physical Sample Number	\bar{b} Reading	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation
A-OL-17-4	1	2.43				
	2	2.12				
	3	2.39	2.31	0.13		
A-OL-17-5	1	1.25				
	2	1.27				
	3	0.90	1.14	0.16		
A-OL-17-6	1	1.08				
	2	1.57				
	3	1.07				
	4	1.08	1.20	0.19	1.79	0.51

*Zinc Diffusion Rate = $\bar{b} \times 10^{-5}$, reported as \bar{b} .

TABLE XL

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A
ZINC DIFFUSION AT 165°F FOR
DIFFERENT BATCHES OF SELECTED FILM
(moles-mil/in²-min)*

Membrane Code	Sample		Batch		Formulation	
	Physical Sample Number	b Reading	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation
A-OL-17-4	1	2.48	2.67	0.19		
	2	2.86				
A-OL-17-5	1	1.86	1.45	0.41		
	2	1.04				
A-OL-17-6	1	1.40	1.26	0.15	1.79	0.59
	2	1.11				

* Zinc Diffusion Rate = $\bar{b} \times 10^{-5}$, reported as \bar{b} .

TABLE XLI

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE B

B-OL-SERIES ZINC DIFFUSION

SPECIFIC IN: moles-mil/in²-min.*; ABSOLUTE IN: moles/in²-min.*

Sample Designation	Composition			Nominal Thickness	77°F			165°F			
					b	Average		b	Average		
	% Inorganic	Organic % Binder	% Plasticize			Specific Readings	Specific		Absolute	Specific Readings	Specific
B-OL-5(W)	80	10 P	10E	7	1.71 1.76	1.74	0.25	1.69 1.58	—	1.64	0.23
B-OL-6(A)	80	10 P	10E	—	—	5.65	0.40	—	—	6.44	0.45
B-OL-7(PP)	80	10 P	10E	10	1.02 0.99 1.04	1.02	0.10	0.87 0.86	—	0.87	0.09

* Zinc Diffusion Rate = $\bar{b} \times 10^{-5}$, Reported as \bar{b} .

NOTE: B-OL-6(A) is the average of several batches.

(See Tables XLII, XLIII and XLIV for Detailed Data and Analysis.)

TABLE XLII

TASK III

COMPOSITE PREPARED BY PROCEDURE B
B-OL-6(A) SERIES ZINC DIFFUSION SUMMARY

Specific = moles-mil/in²-min;* Absolute = moles/in²-min.*

Sample Designation	77°F		165°F	
	Average		Average	
	Specific	Absolute	Specific	Absolute
B-OL-6(A)-1	5.99	0.50	6.91	0.58
B-OL-6(A)-2	5.37	0.34	7.40	0.46
B-OL-6(A)-3	5.58	0.35	5.01	0.31
Average	5.65	0.40	6.44	0.45

*Zinc Diffusion Rate = $\underline{b} \times 10^{-5}$, Reported as \underline{b} .

TABLE XLIII

TASK III: COMPOSITE FILMS (PROCEDURE B)
 ZINC DIFFUSION AT 77°F FOR DIFFERENT BATCHES OF SELECTED FILM
 (moles-mil/in²-min)*

Batch Code	Batch				Formulation	
	Physical Sample No.	Reading	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation
B-OL-6(A)-1	1	6.13				
	2	5.31				
	3	6.54	5.99	0.46		
B-OL-6(A)-2	1	5.54				
	2	4.90				
	3	5.66	5.37	0.31		
B-OL-6(A)-3	1	5.28				
	2	5.87	5.58	0.30	5.65	0.23

*Zinc Diffusion Rate = $\frac{b}{x} \times 10^{-5}$, Reported as $\frac{b}{x}$.

TABLE XLIV

TASK III: COMPOSITE FILMS (PROCEDURE B)
 ZINC DIFFUSION AT 165°F FOR DIFFERENT BATCHES OF SELECTED FILM
 (moles-mil/in²-min)*

Batch Code	Batch				Formulation	
	Physical Sample No.	Reading	Avg. for Physical Sample	Mean Deviation	Average	Mean Deviation
B-OL-6(A)-1	1	7.42				
	2	6.40	6.91	0.51		
B-OL-6(A)-2	1	6.49				
	2	8.30	7.40	0.91		
B-OL-6(A)-3	1	5.32				
	2	4.69	5.01	0.32	6.44	0.95

*Zinc Diffusion Rate = $\frac{b}{x} \times 10^{-5}$, Reported as $\frac{b}{x}$.

TABLE XLV

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A
RESISTANCE TO OXIDATION (SILVER PICK-UP)(Absolute = mg/in²; Specific = mg/in²-mil)

Material Designation	Composition			Days on Stand	77°F			165°F		
	% Inorganic	% Organic Binder	% Plasticizer		Absolute		Specific	Absolute		Specific
					Readings	Average	Average	Readings	Average	Average
Blank-1 (2 mils)	0	50 P	50 E	7	—	—	—	2.12 2.12 3.18	2.47	1.24
				15	2.12 1.06 1.06	1.41	0.71	1.06 2.12 3.18	2.12	1.06
				30	1.06 2.12 3.36	2.18	1.09	4.48 4.48 5.30	4.75	2.38
Blank-2 (2 mils)	0	40 P	60 E	7	1.59 1.06 1.06	1.24	0.62	1.06 1.59 1.06	1.24	0.62
				15	4.24 3.71	3.97	1.98	2.65 3.18	2.92	1.46
				30	4.10 4.64	4.37	2.32			
A-OL-17 (3 mils)	80	10 P	10 E	7	0.63 0.81 0.76	0.67	0.22	8.57 9.79 11.70	10.02	3.34
				15	0.81 0.94 1.10	0.95	0.32	7.97 9.92 12.29	10.06	3.36
				30	1.41 1.28 1.53	1.41	0.47	9.83 11.09 12.40	11.11	3.70
A-OL-18 (3 mils)	90	7.5 P	2.5 E	7	trace trace 1.06	0.18	0.06	2.12 2.65 3.18	2.65	0.88
				15	1.06 1.06 1.06	1.06	0.35	2.12 2.65 2.12	2.30	0.77
				30	*			*		
A-OL-19 (4 mils)	85	10 P	5 E	7	trace trace trace	trace	trace	0.80 0.69 0.74	0.74	0.19
				15	trace trace trace	trace	trace	1.06 0.85 0.90	0.94	0.24
				30	0.25 0.75 0.60	0.58	0.15	*		
A-OL-20 (4 mils)	85	7.5 P	7.5 E	7	trace 0.53 0.53	0.55	0.09	3.71 8.48	6.10	1.52
				15	trace 0.16 0.16	0.11	0.03	*		
				30	1.40 1.51 1.46	1.46	0.37	*		

NOTE: A-OL-17 is the average of several batches (see Tables XLVI and XLVII for detailed data and analysis).

* Samples deteriorated.

TABLE XLVI

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A (A-OL-17 SERIES)
RESISTANCE TO OXIDATION (SILVER-PICK-UP) AT 77°F.(Absolute = mg/in^2) (Specific = $\text{mg/in}^2 \cdot \text{mil}$)
(All Films 3 mil-thick)

Material Designation	Sample			Batch				Formulation		
	Days on Stand	Sample Number	Readings	Absolute		Specific		Absolute	Specific	
				Average	Mean Deviation	Average	Mean Deviation	Average	Average	Mean Deviation
A-OL-17-4	7	1	0.54	0.43	0.07	0.14	0.02	0.67	0.22	0.05
A-OL-17-5		2	0.38							
		3	0.38							
A-OL-17-6		1	0.80	0.81	0.08	0.27	0.03			
		2	0.92							
		3	0.70							
A-OL-17-6		1	0.70	0.76	0.04	0.25	0.01			
		2	0.76							
		3	0.81							
A-OL-17-4	15	1	0.76	0.81	0.03	0.27	0.01	0.95	0.32	0.04
A-OL-17-5		2	0.81							
		3	0.86							
		A-OL-17-6	1	0.81	0.94	0.08	0.31			
2			0.97							
3			1.03							
A-OL-17-6		1	1.08	1.10	0.04	0.37	0.01			
		2	1.13							
		3	1.08							
A-OL-17-4	30	1	1.52	1.41	0.08	0.47	0.03	1.41	0.47	0.03
A-OL-17-5		2	1.40							
		3	1.30							
		A-OL-17-6	1	1.30	1.28	0.10	0.43			
2			1.13							
3			1.40							
A-OL-17-6		1	1.57	1.53	0.03	0.51	0.01			
		2	1.51							
		3	1.51							

TABLE XLVII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE A (A-OL-17 SERIES)
RESISTANCE TO OXIDATION (SILVER PICK-UP) AT 165°F.(Absolute = mg/in^2) (Specific = $\text{mg/in}^2 - \text{mil}$)
(All Films 3 mil-thick)

Material Designation	Sample			Batch				Formulation		
	Days on Stand	Sample Number	Readings	Absolute		Specific		Absolute	Specific	
				Average	Mean Deviation	Average	Mean Deviation	Average	Average	Mean Deviation
A-OL-17-4	7	1	9.67	8.57	0.73	2.86	0.24	10.02	3.34	0.37
A-OL-17-5		2	7.83							
		3	8.21							
A-OL-17-6		1	9.83	9.79	0.26	3.26	0.09			
		2	9.40							
		3	10.15							
A-OL-17-6		1	12.04	11.70	0.14	3.90	0.05			
		2	11.72							
		3	11.34							
A-OL-17-4	15	1	7.45	7.97	0.35	2.66	0.12	10.06	3.36	0.50
A-OL-17-5		2	8.48							
		3	7.99							
A-OL-17-6		1	9.40	9.92	0.35	3.31	0.12			
		2	10.22							
		3	9.94							
A-OL-17-6		1	11.66	12.29	0.44	4.10	0.15			
		2	12.96							
		3	12.26							
A-OL-17-4	30	1	9.99	9.83	0.29	3.28	0.10	11.11	3.70	0.86
A-OL-17-5		2	9.40							
		3	10.10							
A-OL-17-6		1	10.69	11.09	0.26	3.70	0.09			
		2	11.39							
		3	11.18							
A-OL-17-6		1	12.26	12.40	0.22	4.13	0.07			
		2	12.69							
		3	12.26							

TABLE XLVIII

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE B
RESISTANCE TO OXIDATION (SILVER PICK-UP)(Absolute = mg/in²) (Specific = mg/in²-mil)

Material Designation	Composition			Days on Stand	77°F			165°F		
					Absolute		Specific	Absolute		Specific
	% Inorganic	% Organic Binder	% Plasticizer		Readings	Average	Average	Readings	Average	Average
B-OL-5(W) (13 mils)	80	10P	10E	7	trace	trace	trace	4.24	3.89	0.56
					trace	trace	trace	3.71		
					trace	trace	trace	3.71		
B-OL-6(A) (16 mils)	80	10P	10E	15	trace	trace	trace	3.18	3.18	0.45
					trace	trace	trace	3.18		
					trace	trace	trace	3.18		
				30	0.43	0.35	0.05			
					0.27					
B-OL-6(A) (16 mils)	80	10P	10E	7	3.53	5.89	0.39	11.84	9.34	0.64
					7.16			6.79		
					6.98			9.38		
				15	4.24	7.35	0.48	10.25	11.16	0.75
					7.81			10.53		
					10.01			12.71		
B-OL-6(A) (16 mils)	80	10P	10E	30	4.98	8.31	0.54	13.70	12.35	0.84
					9.03			9.30		
					10.91			14.04		

NOTE: B-OL-6(A) is the average of several batches (see Tables iL and L for detailed data and analysis).

TABLE XLIX

TASK III

COMPOSITE FILMS PREPARED BY PROCEDURE B (B-OL-6(A) SERIES)
RESISTANCE TO OXIDATION (SILVER PICK UP) 77°F(Absolute = mg/in²) (Specific = mg/in²-mil)

Material Designation	Days on Stand	Sample		Batch				Formulation		
		Sample Number	Readings	Absolute		Specific		Average	Average	Mean Deviation
				Average	Mean Deviation	Average	Mean Deviation			
B-OL-6(A)-1 (13 mils)	7	1	2.63	3.53	0.60	0.27	0.05	5.89	0.39	0.08
		2	4.24							
		3	3.71							
B-OL-6(A)-2 (16 mils)		1	5.99	7.16	0.78	0.45	0.05			
		2	7.99							
		3	7.51							
B-OL-6(A)-3 (16 mils)		1	8.48	6.98	1.36	0.44	0.08			
		2	4.94							
		3	7.51							
B-OL-6(A)-1	15	1	4.77	4.24	0.35	0.33	0.03	7.35	0.48	0.10
		2	3.71							
		3	4.24							
B-OL-6(A)-2		1	7.34	7.81	0.81	0.49	0.05			
		2	9.02							
		3	7.07							
B-OL-6(A)-3		1	10.58	10.01	0.80	0.63	0.05			
		2	8.80							
		3	10.64							
B-OL-6(A)-1	30	1	5.02	4.98	0.23	0.38	0.02	8.31	0.54	0.11
		2	4.29							
		3	4.64							
B-OL-6(A)-2		1	8.21	9.03	0.81	0.56	0.05			
		2	8.64							
		3	10.26							
B-OL-6(A)-3		1	11.99	10.91	1.19	0.68	0.07			
		2	11.61							
		3	9.13							

TABLE L

TASK-III

COMPOSITE FILMS PREPARED BY PROCEDURE B (B-OL-6(A) SERIES)
RESISTANCE TO OXIDATION (SILVER PICK UP) 1650F(Absolute = mg/in^2) (Specific = $\text{mg/in}^2\text{-mil}$)

Material Designation	Days on Stand	Sample		Batch				Formulation		
				Absolute		Specific		Absolute	Specific	
		Sample Number	Readings	Average	Mean Deviation	Average	Mean Deviation	Average	Average	Mean Deviation
B-OL-6(A)-1 (13 mils)	7	1	11.13	11.84	0.59	0.91	0.04	9.34	0.64	0.18
		2	12.72							
		3	11.66							
B-OL-6(A)-2 (16 mils)		1	7.02	6.79	0.46	0.42	0.03			
		2	6.10							
		3	7.24							
B-OL-6(A)-3 (16 mils)		1	9.23	9.38	0.26	0.59	0.02			
		2	9.13							
		3	9.77							
B-OL-6(A)-1	15	1	10.60	10.25	0.47	0.79	0.04	11.16	0.75	0.06
		2	10.60							
		3	9.54							
B-OL-6(A)-2		1	11.50	10.53	0.83	0.66	0.05			
		2	9.29							
		3	10.80							
B-OL-6(A)-3		1	12.26	12.71	0.30	0.79	0.02			
		2	13.12							
		3	12.74							
B-OL-6(A)-1	30	1	17.33	13.70	2.42	1.05	0.18	12.35	0.84	0.17
		2	11.18							
		3	12.58							
B-OL-6(A)-2		1	10.42	9.30	0.74	0.58	0.05			
		2	9.13							
		3	8.37							
B-OL-6(A)-3		1	14.85	14.04	0.65	0.88	0.05			
		2	14.20							
		3	13.07							

4.4 TASK IV: ONE AMPERE HOUR ZINC-SILVER OXIDE CELL TESTS

The purpose of this task was to determine separator performance in actual cell tests on charged wet stand followed by a high-rate discharge (2C rate). All cells were built as follows:

One silver electrode, 1.6" x 1.6" x 0.022"

Two zinc oxide electrodes, 1.6" x 1.6" x 0.050"

Electrolyte: 31% KOH

Separator: As noted in each group

Test Sequence: Charge: 100 mA to 2.05 V

Discharge: 2 A to 1.0 V

Recharge: 100 mA to 2.05 V

The cell is left on stand and its OCV is monitored daily; the cell is discharged after the requisite period and the residual capacity Q_r and plateau voltage V_r are measured and compared with the original capacity Q_o and plateau voltage V_o . The cell is then recharged, left on stand for 24 hours, to determine that there is no short, then discharged and its actual capacity Q_a and plateau voltage V_a are measured. The capacity retention is calculated as Q_r/Q_o for residual and Q_a/Q_o for actual, whenever the data are available..

4.4.1 Preliminary Tests

Prior to the initiation of the formal test program, preliminary cell tests were run for elimination of preparative defects. The evaluation was concentrated on the dip-coated silver electrode Procedure D. The first two series, P #1 and #2 (Table LI), exhibited wide variations in stand time traceable to the difficulty of coating the electrode edges adequately. This was remedied in the next series which showed immediate improvement (see Group #1 of Paragraph 4.4.2, Table LIII).

4.4.2 Formal Cell Test Plan

Various combinations of separator systems were tested as shown in Table LII. Originally, the plan started with four groups.

Group #1 = Dip coated silver electrodes, formulation 95/5/0

Group #2 = Dip coated silver electrodes, formulation 80/10/10

Group #3 = Bagged zinc electrodes, 80/10/10 on Matrix A

Group #4 = Dip coated Ag; Bagged Zn.

TABLE LI
TASK IV
SCREENING TESTS FOR PREPARATIVE DEFECTS
IN DIP COATED ELECTRODES

Test	Cell Number	Capacity Q ₀ (Ah)	Plateau Voltage V _p at 2A	Wet Stand Days (OCV ≥ 1.84 V)	Remarks
P #1	1-1	1.1	1.22	2	Electrode edges unprotected
	1-2	1.1	1.23	1	
	1-3	1.1	1.28	1	
	1-4	1.0	1.20	8	
	1-5	0.8	1.16	16	
	1-6	1.0	1.26	1	
P #2	2-1	1.0	1.36	Opened for Examination	
	2-2	1.1	1.36	44	Electrode edges unprotected
	2-3	1.2	1.36	1	
	2-4	1.1	1.36	12	
	2-5	1.2	1.36	13	
	2-6	1.1	1.36	59	

TABLE LH
FORMAL TEST PROGRAM PLAN

Separator Fabrication Procedure

Matrix (Bag Construction) B
Coated Ag Electrodes (Dip) D

Formulation

80% Inorganic 3420-09

10% Binder P

10% Plasticizer E

(Except one Group #1, using 95% inorganic and 5% P and no plasticizer)

Number of Cells and Distribution

Group Number	Construction	Formulation	Stand Time (Days)		
			30 d	60 d	90 d
1	Dip coated Ag	95/5/0	3	3	3
2	Dip coated Ag	80/10/10	3	3	6*
3	Bagged Zn	80/10/10 (Matrix A)	3	3	3
4	Dip coated Ag Bagged Zn	80/10/10 (Matrix A)	3	3	3
5	Dip coated Ag Bagged Zn	80/10/10 (Matrix PP)	3		
6	Dip coated Ag Dip coated Zn Dry Charge Plates	80/10/10	3		

These tests were run at 77°F; an equal number of tests were run at 165°F.

*3 with 31% KOH and 3 with 45% KOH.

TABLE LIII

TASK IV

WET STAND

GROUP 1: 95-5-0 DIP-COATED SILVER ELECTRODE

Cell No.	Original		Days at 77°F	Final OCV (V)	Residual		Actual		Capacity Retention	
	Q_o (Ah)	V_o (V)			Q_r (Ah)	V_r (V)	Q_a (Ah)	V_a (V)	$\frac{Q_r}{Q_o}$ (%)	$\frac{Q_a}{Q_o}$ (%)
3.10	1.3	1.23	31	1.86	1.3	1.22	—	—	100	—
3.11	1.2	1.23	31	1.85	1.0	1.17	—	—	83	—
3.12	1.3	1.29	31	1.85	1.2	1.19	—	—	92	—
Avg.	1.3	1.25	31	1.85	1.2	1.19	—	—	92	—
3.13	1.3	1.23	70	1.85	0.9	1.10	1.2	1.25	69	92
3.14	1.3	1.27	70	1.85	0.9	1.19	1.3	1.23	69	100
3.15	1.3	1.23	70	1.85	0.7	1.16	1.2	1.29	54	92
Avg.	1.3	1.24	70	1.85	0.8	1.15	1.2	1.26	64	95
3.16	1.3	1.22	85	1.84	0.3	1.18	0.8	1.28	23	62
3.17	1.3	1.28	85	1.84	0.4	1.21	1.1	1.32	31	85
3.18	1.3	1.31	85	1.84	1.0	1.15	1.2	1.32	77	92
Avg.	1.3	1.26	85	1.84	0.6	1.17	1.0	1.30	44	80

Q_o , V_o = Original capacity and original plateau voltage respectively.

Q_r , V_r = Residual capacity and residual plateau voltage respectively.

Q_a , V_a = Actual capacity and actual plateau voltage after recharge respectively.

In the last month of the program, it was decided to add two new groups for a stand of 30 days.

Group #5 = Equivalent to Group #4, except that a new matrix PP was used in lieu of Matrix A.

Group #6 = Dip coated dry charge electrodes.

The new matrix PP was used in the fabrication of the separator B-OL-7(PP) with the same formulation 80/10/10. Evaluated late at the end of the program, it showed excellent properties in terms of silver and zinc diffusion, but its high resistivity (which can be eventually lowered) was not suitable for a high rate application. Only limited cell tests were performed over 30 days.

The Group #6 using commercial dry charge zinc plates was an attempt to use dip coating on both electrodes. Only 6 cells were tested (3 at 77°F and 3 at 165°F) over 30 days. They all failed on OCV retention except one at room temperature because of the lack of experience of dip coating dry charge silver oxide electrodes and dry charge zinc electrodes in the first attempt.

The stand data at 77°F are presented as follows:

<u>Group</u>	<u>Table</u>
#1	LIII (and Figure 6)
#2	LIV
#3	LV
#4	LVI
#5	LVII

Data for all groups on stand at 165°F are presented in Table LVIII.

Generally, the 77°F stand results show that when capacity loss occurred it was not caused by shorts through separators. At 165°F, the incidence of failures caused by shorts decreased with reinforced separator systems (the groups #4 and #5 have dip coated silver electrodes and bagged zinc electrodes).

4.4.3 Other Tests

Cells left on charged stand for periods up to three months showed a good OCV retention, but sometimes yielded low capacities upon discharge. This was traceable to the capacity loss of the zinc electrode by self-discharge. The silver electrode retained practically all its capacity, and even at 165°F not more than 25% - 30% was lost due to the divalent

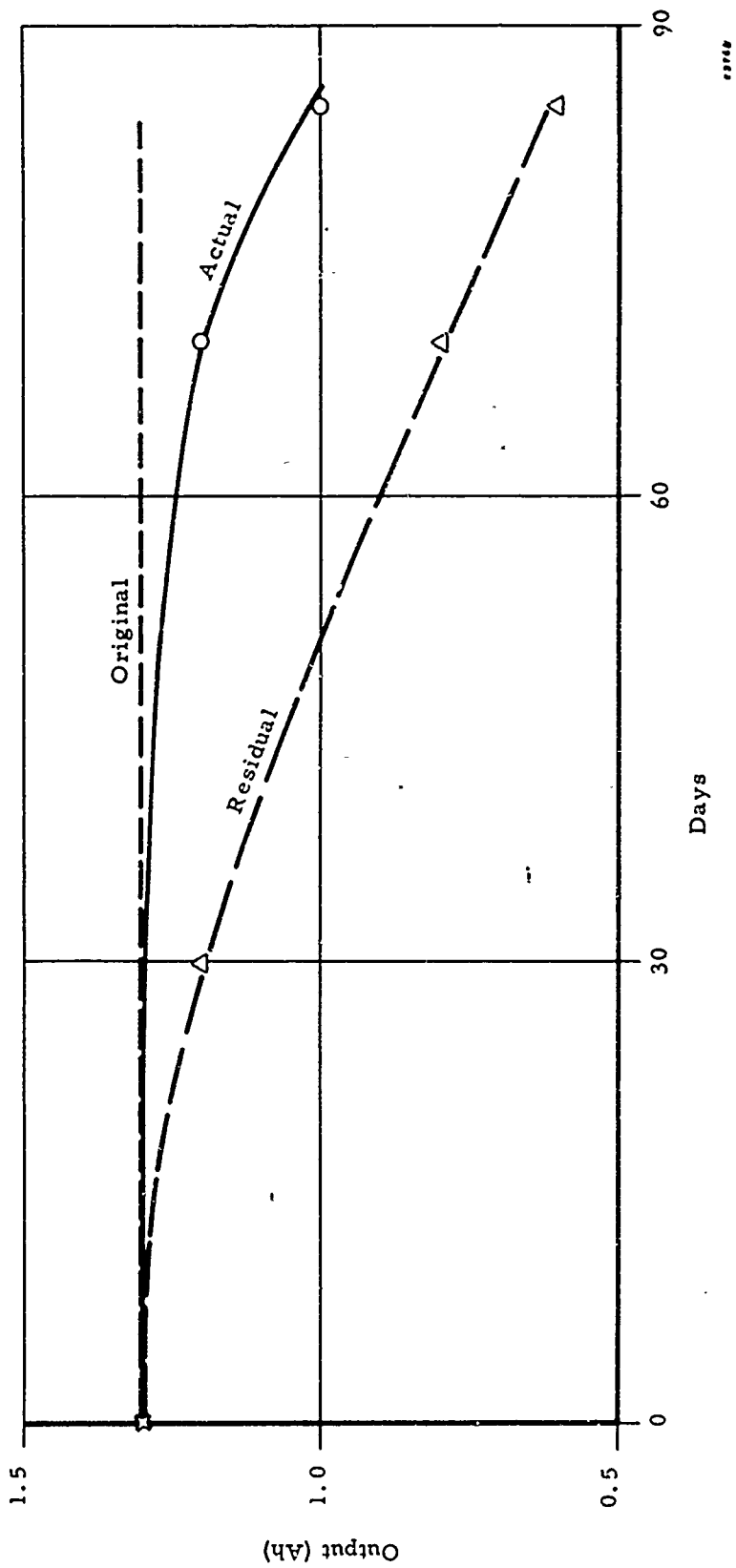


Figure 6. Group 1: Average Output After Wet Stand at 77°F

TABLE LIV

TASK IV

WET STAND - GROUP 2
80-10-10 DIP-COATED SILVER ELECTRODE

Cell Number	Original		Days at 77°F	Final OCV (V)	Residual		Actual		Capacity Retention	
	Q _o (Ah)	V _o (V)			Q _r (Ah)	V _r (V)	Q _a (Ah)	V _a (V)	Q _r /Q _o (%)	Q _a /Q _o (%)
387	1.4	1.41	34	1.86	1.2	1.36	1.4	1.38	86	100
388	1.4	1.39	34	1.86	1.1	1.34	1.4	1.34	79	100
389	1.3	1.39	Failed at 17 days		—	—	—	—	—	—
Average	1.4	1.40	34	1.86	1.2	1.35	1.4	1.36	83	100
390	1.3	1.41	59	1.84	0.1	1.11	—	—	8	—
391	1.5	1.39	59	1.86	0.6	1.32	0.9	1.37	40	60
392	1.3	1.40	59	1.86	0.8	1.32	1.1	1.36	62	85
Average	1.4	1.40	59	1.85	0.5	1.25	1.0	1.37	37	73
393	1.4	1.40	Failed at 37 days		—	—	—	—	—	—
394	1.3	1.39	90	1.83	0.7	1.32	1.0	1.36	54	77
395	1.3	1.40	Failed at 72 days		—	—	—	—	—	—
Average	1.3	1.40								
396*	1.2	1.26	90	1.86	0.7	1.20	1.2*	1.30	58	100
397*	1.2	1.26	90	1.86	0.3	1.08	0.9*	1.25	25	75
398*	1.2	1.29	90	1.86	0.5	1.13	1.1*	1.28	42	92
Average	1.2	1.27	90	1.86	0.5	1.14	1.1	1.28	42	90

* Cells were filled with 45% KOH instead of the usual 31% KOH and were purposely overcharged.

Q_o, V_o = Original capacity and original plateau voltage, respectively.

Q_r, V_r = Residual capacity and residual plateau voltage, respectively.

Q_a, V_a = Actual capacity and actual plateau voltage after recharge, respectively.

TABLE LV
TASK IV
WET STAND - GROUP 3
BARE SILVER ELECTRODE;
BAGGED ZINC ELECTRODES (MATRIX A)

Cell Number	Original		Days at 77°F	Final OCV (V)	Residual		Actual		Capacity Retention	
	Q _o (Ah)	V _o (V)			Q _r (Ah)	V _r (V)	Q _a (Ah)	V _a (V)	Q _r /Q _o (%)	Q _a /Q _o (%)
487	1.3	1.33	28	1.86	0.9	1.27	0.9	1.27	69	69
488	1.2	1.30	28	1.86	0.8	1.27	1.0	1.26	67	83
489	1.3	1.30	28	1.86	1.0	1.28	1.0	1.28	77	77
Average	1.3	1.31	28	1.86	0.9	1.27	1.0	1.27	71	76
490	1.5	1.32	61	1.86	1.1	1.30	1.2	1.30	73	80
491	1.4	1.31	61	1.86	0.7	1.25	0.8	1.27	50	57
492	1.5	1.32	61	1.85	0.6	1.19	0.7	1.25	40	47
Average	1.5	1.32	61	1.86	0.8	1.25	0.9	1.27	54	61
493	1.1	1.29	85	1.86	0.7	1.27	1.0*	1.29	64	91*
494	1.4	1.31	85	1.86	0.6	1.25	0.7	1.31	43	50
495	1.4	1.31	85	1.85	0.3	1.19	0.7	1.30	21	50
Average	1.3	1.30	85	1.86	0.5	1.24	0.8	1.30	43	64

Q_o, V_o = Original Capacity and Original Plateau Voltage, respectively.

Q_r, V_r = Residual Capacity and Residual Plateau Voltage, respectively.

Q_a, V_a = Actual Capacity and Actual Plateau Voltage after recharge, respectively.

* = Cell was purposely overcharged.

TABLE LVI

TASK IV

WET STAND - GROUP 4
DIP-COATED SILVER ELECTRODE;
BAGGED ZINC ELECTRODES (MATRIX A)

Cell Number	Original		Days at 77°F	Final OCV (V)	Residual		Actual		Capacity Retention	
	Q _o (Ah)	V _o (V)			Q _r (Ah)	V _r (V)	Q _a (Ah)	V _a (V)	Q _r /Q _o (%)	Q _a /Q _o (%)
469	1.3	1.25	30	1.86	0.5	1.20	0.8	1.25	38	62
470	1.3	1.24	30	1.86	0.7	1.22	0.9	1.26	54	69
471	1.2	1.25	30	1.86	0.5	1.21	0.8	1.25	42	67
Average	1.3	1.25	30	1.86	0.6	1.21	0.8	1.25	45	66
472	1.3	1.35	59	1.85	0.3	1.16	0.8	1.25	23	62
473	1.2	1.24	59	1.84	0.2	1.15	0.7	1.24	17	58
474	1.1	1.24	59	1.85	0.2	1.16	0.7	1.23	18	64
Average	1.2	1.24	59	1.85	0.2	1.16	0.7	1.24	19	61
475	1.2	1.20	90	1.86	0.3	1.15	0.7	1.20	25	58
476	1.2	1.25	90	1.86	0.3	1.18	1.1*	1.25	25	92*
477	1.4	1.26	90	1.86	0.5	1.20	1.1*	1.26	36	79*
Average	1.3	1.24	90	1.86	0.4	1.18	1.0	1.24	29	76

Q_o, V_o = Original Capacity and Original Plateau Voltage, respectively.

Q_r, V_r = Residual Capacity and Residual Plateau Voltage, respectively.

Q_a, V_a = Actual Capacity and Actual Plateau Voltage after recharge, respectively.

* = Cells were purposely overcharged.

TABLE LVII

TASK IV

WET STAND - GROUP 5
 80/10/10 DIP-COATED SILVER ELECTRODE;
 BAGGED ZINC ELECTRODES (MATRIX PF)

Cell Number	Original		Days at 77°F	Residual		Actual		Capacity Retention	
	Q_o (Ah)	V_o (V)		Q_r (Ah)	V_r (V)	Q_a (Ah)	V_a (V)	$\frac{Q_r}{Q_o}$ (%)	$\frac{Q_a}{Q_o}$ (%)
M-1	1.0	1.10	30	0	1.85	1.0	1.15		100
M-2	1.0	1.15	30	0.5	1.85	1.0	1.15	50	100
M-3	1.0	1.14	30	0.4	1.86	1.0	1.18	40	100
Average	1.0	1.13	30	0.5	1.85	1.0	1.16	45	100

Q_o, V_o = Original Capacity and Original Plateau Voltage, respectively.

Q_r, V_r = Residual Capacity and Residual Plateau Voltage, respectively.

Q_a, V_a = Actual Capacity and Actual Plateau Voltage After recharge, respectively.

TABLE LVIII
TASK IV
WET STAND AT 165°F - SUMMARY

Group Number	Cell Number	Original at 77°F		Days OCV $\geq 1.62V$ at 165°F Stand	Residual at 77°F		OCV Check Day(s)** Before Discharge	Actual at 77°F		% Survival
		Q _o (Ah)	V _o (V)		Q _r (Ah)	V _r (V)		Q _a (Ah)	V _a (V)	
#1 (dip-coated silver) 95/5/0	301	1.3	1.25	24	0		1	1.3	1.25	
	302	1.1	1.26	14	F					
	303	1.2	1.26	18	F					
	304	1.2	1.26	22	0.6	1.22	2	0.8	1.24	
	305	1.2	1.31	22	0.2	1.15	F			
	306	1.1	1.23	9	F					
	307	1.2	1.25	22	0.3	1.19	F			
	308	1.4	1.34	18	F					
	309	1.1	1.25	4	F					
Average		1.2	1.26					1.05	1.24	22%
#2 (dip-coated silver) 80/10/10	378	1.5	1.42	10	0.2	1.20	1	0.7	1.34	
	379	1.5	1.41	9	0.3	1.20	1	0.8	1.30	
	380	1.3	1.41	10	0		1	0.7	1.32	
	381	1.6	1.40	6	F					
	382	1.5	1.41	6	F					
	383	1.3	1.39	10	0.5	1.20	1	1.1	1.37	
	384	1.4	1.41	8	0.1	1.15	F			
	385	1.3	1.39	9	F					
	386	1.3	1.41	8	F					
Average		1.4	1.40					0.8	1.33	44%
#3 (Bagged Zn)	557	1.5	1.36	5	0		1	1.5	1.36	
	558	1.5	1.37	1	0.8	1.10	F			
	559	1.5	1.37	7	0		F			
	560	1.5	1.37	7	0		3	1.4*	1.36	
	561	1.5	1.36	13	0.3	1.30	1	1.6*	1.36	
	562	1.5	1.35	7	0		3	1.4*	1.38	
	563	1.5	1.35	1	F					
	564	1.5	1.36	7	0		3	1.5*	1.37	
	565	1.5	1.35	5	0		1	1.4*	1.38	
Average		1.5	1.36					1.5	1.36	66%

(Continued)

TABLE LVIII (Continued)

TASK IV

WET STAND AT 165°F - SUMMARY

Group Number	Cell Number	Original at 77°F		Days OCV $\geq 1.62V$ at 165°F Stand	Residual at 77°F		OCV Check Day(s)** Before Discharge	Actual at 77°F		% Survival
		Q _o (Ah)	V _o (V)		Q _r (Ah)	V _r (V)		Q _a (Ah)	V _a (V)	
#4 (Dipped Ag Bagged Zn) (Matrix A)	575	1.1	1.25	6	0.2	1.10	1	0.7	1.24	
	576	1.2	1.34	6	0		3	1.3*	1.35	
	577	1.2	1.27	6	0.4	1.20	1	1.5*	1.33	
	578	1.2	1.34	4	0.7	1.29	3	1.3*	1.33	
	579	1.2	1.32	6	0.3	1.15	1	1.5*	1.36	
	580	1.1	1.35	6	0.3	1.20	1	1.6*	1.35	
	581	1.3	1.31	5	0.8	1.30	3	1.5*	1.35	
	582	1.1	1.35	6	0.4	1.20	1	0.7*	1.35	
	583	1.2	1.30	4	0		1	0.5	1.25	
Average		1.2	1.34					1.2	1.32	100%
#5 (Dipped Ag Bagged Zn) (Matrix PP)	M-4	0.7	1.20	13	0		1	1.2	1.24	
	M-5	1.0	1.22	13	0		1	1.1	1.18	
	M-6	1.0	1.23	4	0.7	1.20	1	1.0	1.20	
Average		0.9	1.22					1.1	1.21	100%

* = Cells were purposely overcharged.

** = Cells were recharged and held at OCV = 1.86 for the reported number of days before final discharge.

F = Cells had no capacity, would not accept a charge, or could not hold OCV for 24 hours.

silver oxide decomposition. In some instances, after the discharge was completed, the cell was force-discharged (by reversal) and yielded a capacity of about 0.8 to 0.9 Ah before the gassing and electrolyte decomposition potential was reached.

4.4.3.1 Silver Plate Tests

To establish and separate the contribution factors, charged silver electrodes were placed in KOH at 77°F and 165°F for periods of 1, 2, and 3 months, and discharged after each requisite period. Some plates were dip-coated with each of the formulations 95/5/0 and 80/10/10. Some were uncoated. The data presented in Tables LIX and LX shows the relatively good capacity retention at room temperature with plates even dip-coated and the expected loss of 20 to 30% for plates stored at 165°F.

4.4.3.2 Overcharge Tests

In the long wet stand series of the last groups, some cells were purposely overcharged for the determination of their actual capacity Q_a after stand in an attempt to bring up the zinc electrode capacity which seemed to be the limiting factor. These cells gave capacities higher than cells of shorter wet stand not submitted to this treatment.

4.4.3.3 Dry-Charge Zinc Plate Tests

Some dry-charge zinc electrodes were left in KOH at 77°F and 165°F for about 30 days. Their capacities were compared against the original capacity of identical fresh plates. The results were as follows:

<u>Days On Stand</u>	<u>Temperature</u>	<u>Capacity</u>	<u>Capacity Retention</u>
0	77°F	8.3 Ah	--
29	77°F	7.4 Ah	90%
26	165°F	3.2 Ah	38%

It appears that at 165°F the self-discharge phenomenon is accelerated, whereas at 77°F, the capacity retention is relatively good (10% loss per month).

The self-discharge experienced in test cells is therefore caused partly by the natural loss of capacity standing in KOH over a long period of time and partly by possible impurities coming from the matrix supporting the inorganic film, since cells without matrix did not lose so much capacity.

TABLE LIX

TASK IV

CHARGED SILVER PLATE WET STAND TESTS AT 77°F

(Fixed Input = 1.20 Ah)

Plate No.	Type of Coating	Stand KOH Conc (%)	Days on Stand	Final OCV (V)	Output (Ah)	Average Output (Ah)
SA 1-1	80/10/10	31	28	1.63	0.81	0.93
1-2	80/10/10	31	28	1.83	0.98	
1-3	80/10/10	31	28	1.86	1.00	
SA 8-1	95/5/0	31	28	1.86	1.03	1.17
8-2	95/5/0	31	28	1.86	1.30	
SA 14-1	None	31	28	1.86	1.10	1.10
SA 20-1	None	45	28	1.86	1.10	1.10
SA 2-1	80/10/10	31	52	1.66	0.90	0.91
2-2	80/10/10	31	52	1.86	0.92	
2-3	80/10/10	31	52	1.86	0.90	
SA 9-1	95/5/0	31	52	1.86	0.95	0.95
SA 15-1	None	31	52	1.86	0.98	0.98
SA 21-1	None	45	52	1.86	1.08	1.08
SA 3-1	80/10/10	31	83	1.78	0.85	0.90
3-2	80/10/10	31	83	1.66	0.84	
3-3	80/10/10	31	83	1.86	1.00	
SA 10-1	95/5/0	31	83	1.66	0.83	0.82
10-2	95/5/0	31	83	1.65	0.80	
SA 16-1	None	31	83	1.86	1.12	1.12
SA 22-1	None	45	83	1.86	1.12	1.12

NOTE: OCV measured against freshly cleaned zinc wire.

TABLE LX

TASK IV

CHARGED SILVER PLATE WET STAND TESTS AT 165°F

(Fixed Input = 1.20 Ah)

Plate No.	Type of Coating	Stand KOH Conc (%)	Days on Stand	Final OCV (V)	Output (Ah)	Average Output (Ah)
SA 4-1	80/10/10	31	30	1.63	0.87	0.88
4-2	80/10/10	31	30	1.63	0.84	
4-3	80/10/10	31	30	1.63	0.92	
SA 11-1	95/5/0	31	30	1.63	0.80	0.80
11-2	95/5/0	31	30	1.63	0.80	
SA 17-1	None	31	30	1.64	0.95	0.95
SA 23-1	None	45	30	1.64	0.95	0.95
SA 5-1	80/10/10	31	52	1.64	0.90	0.90
5-2	80/10/10	31	52	1.63	0.90	
5-3	80/10/10	31	52	1.64	0.90	
SA 12-1	95/5/0	31	52	1.64	0.98	0.97
12-2	95/5/0	31	52	1.64	0.95	
SA 18-1	None	31	52	1.60	0.98	0.98
SA 24-1	None	45	52	1.64	0.98	0.98
SA 6-1	80/10/10	31	83	1.66	0.80	0.78
6-2	80/10/10	31	83	1.65	0.83	
6-3	80/10/10	31	83	1.65	0.70	
SA 7-1	80/10/10	45	83	1.65	0.83	0.84
7-2	80/10/10	45	83	1.64	0.85	
SA 13-1	95/5/0	31	83	1.66	0.87	0.85
13-2	95/5/0	31	83	1.65	0.82	
SA 19-1	None	31	83	1.66	0.85	0.85
SA 25-1	None	45	83	1.66	0.87	0.87

NOTE: OCV measured against freshly cleaned zinc wire.

Section 5

CONCLUSIONS AND RECOMMENDATIONS

The program was devoted to evaluating a suitable separator material in terms of resistivity, inertness in KOH, silver and zincate diffusion and resistance to silver oxidation.

One inorganic material 3420-09 in powder form was selected, an adequate binder P known to be completely inert in KOH was used to hold the inorganic particles and a plasticizer E served to give elastomeric properties to the film either cast or deposited on a matrix or on electrodes.

The optimum formulation appears to be 80% inorganic, 10% binder and 10% plasticizer. The resistivity was in the low range of 10 to 15 ohm-cm, the stability in KOH was found acceptable, the silver and zincate diffusion rates relatively low and the resistance to oxidation good.

In cell tests, the incidence of failures caused by mechanical cracks in the texture of the separator was found to be worst only at 165°F in the case where dip-coated silver electrodes were exclusively used.

It is revealing that such a separator material can be used in various forms at a desired thickness and porosity level to make it fit any cell design (scale-up) or mission application.

The present state-of-the-art for primaries covers (1) automatically activated batteries capable of very high rates, but very short wet stand (hours), always with a doubt as to their reliability after a period of 2 to 3 years dry storage; (2) nonreserve manually activated batteries capable of medium to high rate, but of still short wet stand (days); (3) nonreserve, manually activated batteries capable of only low rates and long wet stands (months), but still not capable of retaining their full capacity which decreases with stand time and stand temperature.

Consequently, there is a need for nonreserve primaries capable of both high rate and long wet stand with minimal capacity loss.

The evaluation of inorganic-organic separators for alkaline cells cannot be complete without testing actual cells using properly designed components, and directly comparing these with the best systems commercially available in order to compensate for the effects of the components other than the separators. Stand time and high rate performance can be directly compared between competitive separators.

It may be that from such tests other meaningful information will be derived, for instance, the use of a separator for a long wet stand, non-reserve primary capable of limited recycling for checking purposes

and nondestructive testing. This feature may compensate for any other shortcoming which does not bring the new material completely to par with established materials yielding high voltages at high rates but having relatively short wet stand.

Several parameters should be considered — charged and discharged wet stand, wide range of temperature with occasional excursions up to 200°F, high rate performance for capacity and voltage, capability of limited recycling, effect of trickle charge to maintain capacity over long periods and still prevent zinc dendrite penetration (resulting in shorts and premature failures), effect of pulse, periodic and asymmetric charge techniques as maintenance means after long intervals of stand.

It is therefore recommended that such a program be initiated to evaluate the new separator material against present state-of-the-art materials.

Appendix A

METHODS FOR BATTERY SEPARATOR MEASUREMENTS

A.1 RESISTIVITY

This measurement is performed according to the method of Salkind and Kelly.* An AC method is used. The set-up is shown in Figure A-1. The sample is vacuum impregnated for at least 30 minutes in 31% KOH.

The voltage drop across two fixed platinized platinum electrode tips is measured. The resistance is first obtained for the electrolyte from the measurement of voltages at various currents. Voltage is plotted against current, the slope of the line gives the resistance R_e .

Then, the separator sample is inserted and the voltage-current relationship is determined, giving an overall resistance R_s . The resistance of the separator R is then:

$$R = R_s - R_e$$

The resistivity of the separator ρ in ohm-cm is then:

$$\rho = \frac{Ra}{t}$$

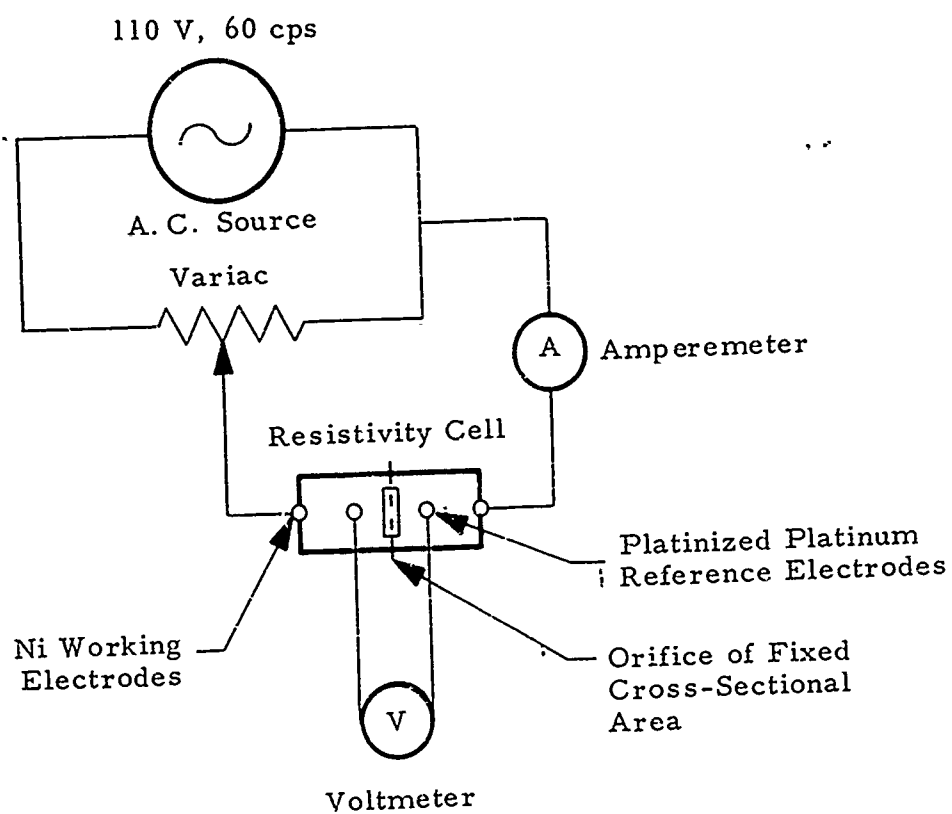
where a is the cross-sectional area of the active separator in cm^2 and t is the separator thickness in cm.

A.2 TRANSVERSE STRENGTH OF INORGANIC SEPARATORS

Samples are broken on the transverse testing machine shown in Figure A-2. The modulus of rupture was calculated according to the equation:

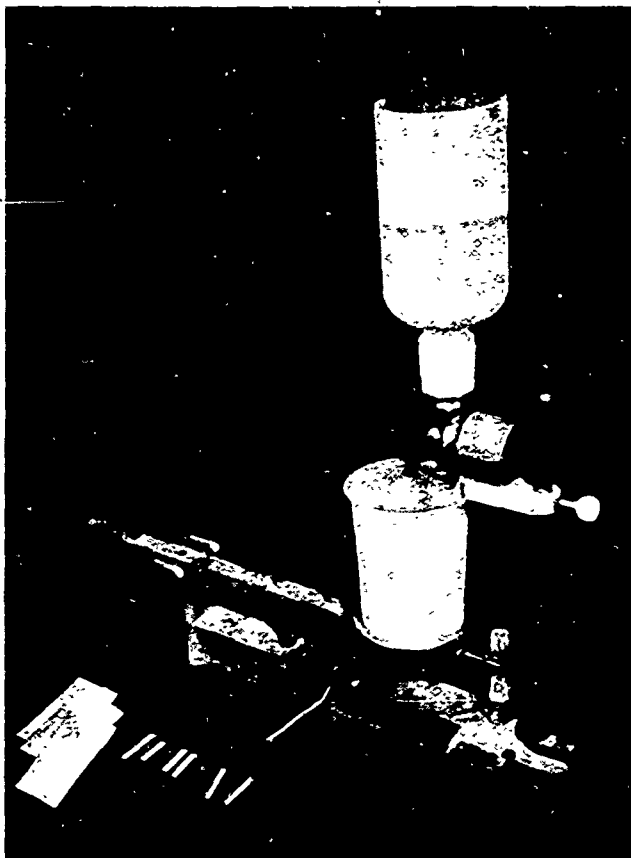
$$M = \frac{3Pl}{2bd^2}$$

*Salkind, A. J. and J. J. Kelly, "Electrical Resistance-Alternating Current Method," Characteristics of Separators for Alkaline Silver Secondary Batteries, Edited by J. E. Cooper and A. Fleisher, Air Force Aero Propulsion Laboratory, p. 69.



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Figure A-1. Schematic of Resistivity Measuring Apparatus



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Figure A-2. Transverse Strength Apparatus

where,

M = modulus of rupture (psi)

P = breaking load (pounds)

b = breadth (inches)

l = span (inches)

d = thickness (inches)

Tested specimens have the following measurements:

b = 1/2 inch

l = 1 inch

Formula used:

$$M = \frac{3P}{d^2}$$

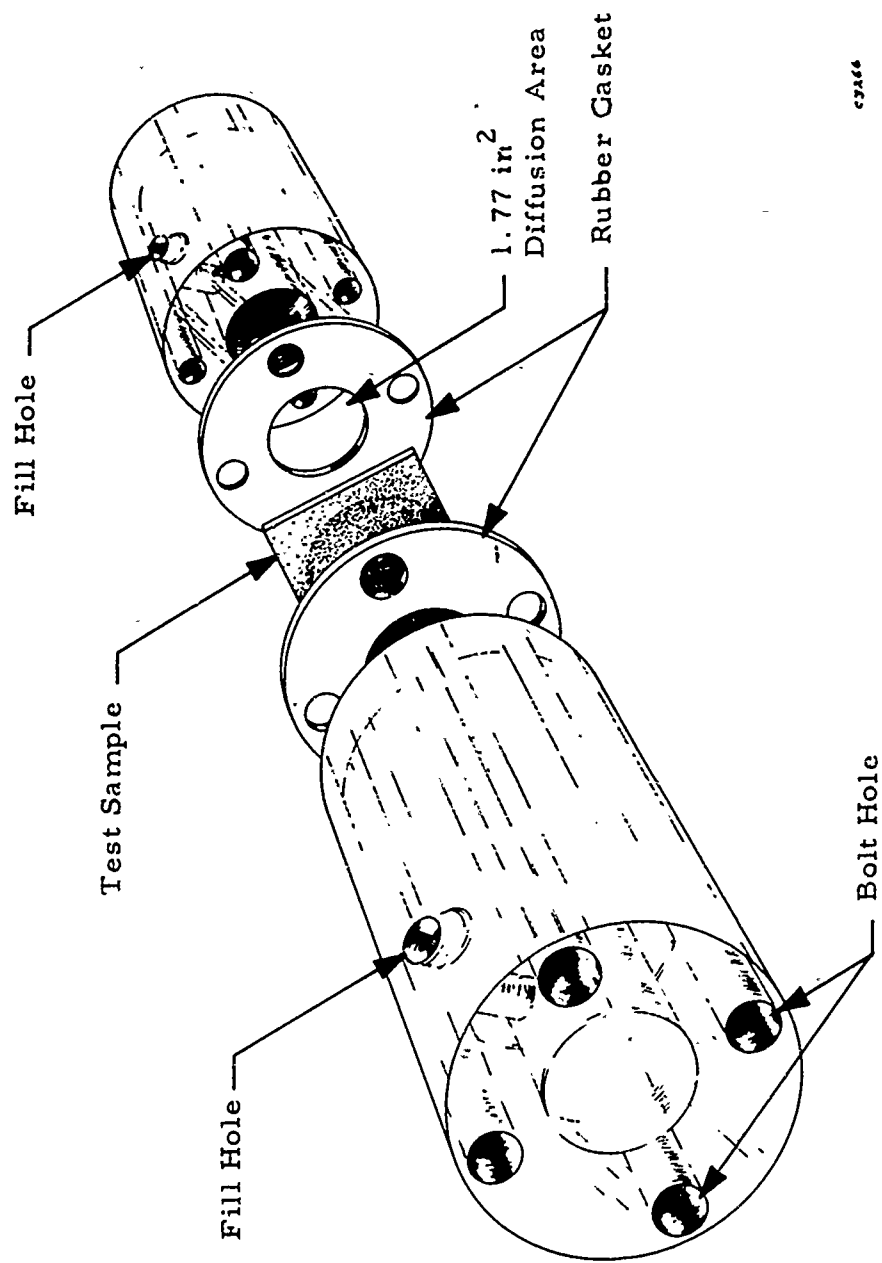
A.3 SILVER DIFFUSION

The measurement of separator impermeability to silver ions in 31% KOH solution is performed in the Lucite diffusion apparatus shown in Figure A-3. After the separator is vacuum impregnated at 29 inches Hg with 31% KOH solution for at least one half hour, it is installed in the diffusion apparatus between rubber gaskets as shown in Figure A-3. Both halves of the apparatus are bolted together. The primary side (100 ml volume) is filled with a saturated solution of silver oxide in 31% KOH solution. Then, the secondary side (50 ml volume) is filled with 31% KOH solution. Charged dipped electrodes are just placed in 50 ml of 31% KOH.

At two-hour intervals, a one-ml sample is pipetted from the secondary compartment and is analyzed for silver by the following colorimetric analysis.

A 1-ml sample is placed in a 25-ml volumetric flask to which 5.0 ml of 1.65 N nitric acid has been added. Distilled water is added to bring the level up to just below the neck of the flask (23-24 ml); then 1.0 ml of 0.05 % rhodanine solution is added. Finally, it is filled up to the mark with distilled water.

A Klett-Summerson Photoelectric Colorimeter is used in the analysis. The colorimeter sample tube is rinsed twice with approximately 5 ml of the above sample before being filled with 10 ml of the sample for the absorption measurement. Before each absorption reading, the colorimeter is zeroed with a blank solution of the rhodanine in 31% KOH. The



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Figure A-3. Silver and Zinc Diffusion Apparatus

concentration of the silver ions is read directly from a calibration curve. Generally, readings were taken after two, four, and six hours and the rate was calculated over the six-hour period. For relatively rapid diffusion rates, the rates were calculated over two or four hours. For extremely low rates of diffusion, the experiment was performed over a longer period.

The average variation of concentration per hour is noted $G = \frac{\Delta C}{\Delta T}$ (mg/l)/hr. The rate of silver diffusion is the amount diffusing per hour through one square inch of separator one mil thick.

$$a = \frac{G \cdot t \times 50}{1000 A} \quad (\text{mg} - \text{mil}/\text{in}^2 - \text{hr})$$

where,

t = thickness of separator in mils

A = area of separator in in^2 (1.77 in^2)

A.4 ZINCATE DIFFUSION

The diffusion apparatus is the same as that described for silver diffusion (see also Figure A-3), except that the volume of the secondary compartment is 100 ml. The following procedure was used:*

The separator sample is vacuum impregnated at 29 inches Hg with 31% KOH solution for 30 minutes. Then the sample is assembled with the diffusion cell. A stirring bar is placed in the secondary side and 1.0 ml of 0.1 M ZnO_2 in 31% KOH solution is added. Then, the secondary side is filled with 31% KOH solution and an amalgamated zinc strip and Hg-HgO reference electrode is inserted. A constant voltage power source is connected in opposition with the reference electrode. The tip of an argon purge tube is placed through the hole in the top of the diffusion apparatus close to the zinc strip, but above the solution.

The rich-zinc side of the apparatus is filled with saturated zincate solution of 31% KOH. The solution on the secondary side is stirred.

After 30 minutes, a reading of the difference in potential is made between the reference electrode and the partially immersed zinc strip. The measurement is repeated every 60 minutes over a period of four hours.

*Lander, J. J., "Zinc Diffusion," *ibid*, p. 115.

The concentration of zincate ion is obtained from a calibration curve giving correspondence of concentration and voltages.

The average variation of concentration per minute is noted $G = \frac{\Delta C}{\Delta T}$ in (moles/l)/minute.

The rate of zincate diffusion is the amount of diffusion per minute through one square inch of separator one mil thick.

$$B = b \cdot 10^{-5} = \frac{G \cdot t \times 100}{1000 \times A} \quad (\text{in moles-mil/in}^2\text{-minute})$$

where,

t = thickness of separator in mils

A = area of separator in in^2 (1.77 in^2)

In order to simplify the tables, the factor b is given in the course of the report.

A. 5 SILVER PICK-UP*

Samples of one square inch cross-sectional area are suspended in a saturated solution of silver oxide in 31% KOH solution. The samples at 77°F are kept in stoppered polyethylene bottles. The tests at 165°F are kept in polysulfone cases. The volume of electrolyte used is 50 ml. After the requisite stand time, the sample is removed, washed several times with distilled water until neutral, and placed in a beaker containing 25 ml of 1:2 nitric acid. The sample is heated gently for one-half hour. Then 5 ml of ferric ammonium indicator is added and the sample is titrated with 0.01 N KCNS to a rust colored end-point. The amount of silver pick-up is determined in mg/in^2 .

*Lander, J. J., "Degradation of Soluble Silver," *ibid*, p. 77.

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13. ABSTRACT <p>This report covers a program on the investigation of separator materials for high rate, nonreserve zinc-silver oxide batteries capable of operating at temperatures as high as 165°F.</p> <p>The films were obtained by blending an inorganic material (previously used to make separators for secondary silver-zinc cells) with an organic binder.</p> <p>The program consisted of four tasks:</p> <ol style="list-style-type: none">1. <u>Characterization of Inorganic Materials</u> Two basic materials, designated 3355-25 and 3420-09, were selected to make separators which were used as controls and were evaluated for resistivity, inertness in KOH at 77°F and at 165°F, silver and zinc diffusion rates and resistance to oxidation by silver saturated KOH solution. Although both materials showed close characteristics, the material 3420-09 was selected for its greater stability in KOH at 165°F.2. <u>Initial Composite Film Preparation and Characterization</u> For blending, two types of organic binders, K and P, and three procedures were used: Procedure A: The film was cast on glass or Teflon. Procedure B: A slurry was introduced in a porous thin matrix. Procedure D: The silver electrode was dipped in the liquid formulation, resulting in a dip-coated electrode. The results favored the binder P as more stable. The resistivities of the most promising films were in the range of 7 to 15 ohm-cm and the silver ion diffusion rates were lower than those obtained with the inorganic separators on the previous task.3. <u>Final Composite Film</u> This task was aimed at continued improvement and evaluation of certain films selected from the previous task. One formulation was found worth using by two procedures, A and B, and the membranes prepared by these two procedures were extensively evaluated for uniformity and fabrication reproducibility.4. <u>Cell Testing and Evaluation</u> Several wet stand tests were run on cells of various separator designs and combinations. All cells were identical in electrode design and had 1-Ah nominal capacity. The separator system used involved exclusively silver electrode dip-coating, zinc-bagging, or both. All systems were potentially good over a period of 3 months at room temperature. At 165°F, the maximum reliability was attained by combining Ag dip-coating and Zn bagging. Loss of capacity at 165°F was traced to zinc capacity loss rather than separator deficiency and shorting.		

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